Bond Orders and Electric Quadrupole Moments for Ethane, Ethylene, and Acetylene from a Point-Charge Model[1]

Raymond F. Borkman* and Frank A. Settle, Jr.[2]

Contribution from the School of Chemistry, Georgia Institute of Technology, Atlanta, Georgia 30332, and Department of Chemistry, Virginia Military Institute, Lexington, Virginia 24450. *Received March 3, 1971*

Abstract: A point-charge model is developed and used to describe the electronic structures of ethane, ethylene, and acetylene. For each molecule, positive point charges representing the screened nuclei are located at the positions of the nuclei, and negative point charges representing the valence electrons are located between pairs of nuclei. These point charges are evaluated, *via* a formalism based on the scaled form of the polyatomic virial theorem, by requiring the Coulomb potential associated with interaction of the system of charges to exactly reproduce the values of empirical vibration force constants. Thus, the model uses experimental force constants and molecular geometries as input and yields a crude picture of the molecular electronic structure as output. The magnitudes of the point charges representing the valence electrons in a particular bond ("bond charges") provide an empirical measure of the "bond order" appropriate to that bond. For acetylene, ethylene, and ethane, respectively, the model yields C–C bond orders of 2.9, 2.2, and 1.2 and C–H bond orders of 1.0, 1.1, and 1.2. Once the complete system of nuclear and bond charges has been evaluated for a given molecule, classical electrostatics can be used to compute electric multipole moments for that molecule. Electric quadrupole moments calculated for the three C_2H_{2n} molecules are found to be uniformly larger than literature values, but the signs and relative magnitudes are correctly predicted by the model.

Some electronic properties of molecules such as ground-state electric dipole moments can be measured with relative ease using established methods. Other electronic properties, including, for example, dipole moments of electronically excited molecules[3] and electric quadrupole moments,[4] are not so readily obtained, either from experiment or theory. In contrast, vibrational properties of many molecules have been extensively studied and tabulated,[5] often for several electronic states of the same molecule. It is reasonable therefore to inquire into the feasibility of using molecular vibrational data to deduce simple molecular electronic properties. What we require is a theoretical model for translating molecular vibration language into electronic structure language.

Recently there has been interest in point-charge models as probes into the relationship between vibrational force constants and electronic properties. A "bond-charge" model was developed previously and applied to a large number of homonuclear[6] and heteronuclear[7] diatomic molecules. This model was based on the molecular virial theorem and gave a prescription whereby bond stretching force constants were used as input data to generate a system of point charges, one set of charges representing the screened nuclei and another representing the valence electrons. This system of charges was chosen so as to exactly reproduce the experimental force constant. Knowledge of the magnitude and location in space of the point charges permitted evaluation of electric dipole and quadrupole moments; in addition, an empirical estimate of the bond order of the molecule was obtained.[6–10]

Work has been done on extending the above model to polynuclear systems. Martin[11] has used the point-charge system reported for the C_2 molecule[6] to treat lattice vibrations in the diamond crystal. Other related work on solids has also appeared.[12] Parr and Brown[13] and Nelander[14] have derived a form of the polyatomic virial theorem suitable for extending the bond-charge model to general systems, and Takahata and Parr have used these results to discuss molecular bending.[15] Borkman has applied the bond-charge model to polyatomic molecules of the XY_n type.[8] In the present paper we extend this XY_n bond-charge model to include molecular structures of the type X_2Y_{2n} and use available vibrational data for ethane, ethylene, and acetylene to deduce bond orders and electric quadrupole moments for these molecules.

Theoretical Section

Virial Theorem for Scaled Motion. The development here is similar to that given previously for XY_n molecules.[8] We consider a molecular structure to be given in terms of a set of independent internuclear distances, $\{R_i\} = R_1, R_2, \ldots, R_n$, and a set of bond angles, $\{\theta_i\} = \theta_1, \theta_2, \ldots, \theta_m$. For a scaled motion of the molecule[16] we have $R_i = R_i^0S$, and $\theta_i = \theta_i^0$, for all values of i, where R_i^0 and θ_i^0 refer to the equilibrium geometry of the molecule and S is the scale parameter. For such motions the electronic kinetic energy, T, the potential energy, V, and the total energy, W, are functions only of the equilibrium quantities $\{R_i^0\}$ and $\{\theta_i^0\}$ and the scale parameter S, and the molecular

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[1] Supported in part by the National Science Foundation.

[2] National Science Foundation Summer Research Participant at Georgia Institute of Technology, Summer, 1969.

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virial theorem can be written as

$$S\,\mathrm{d}W/\mathrm{d}S + 2W = V \tag{1}$$

Differentiating eq 1 with respect to S and evaluating at the equilibrium geometry yields

$$K_{\mathrm{sym}} \equiv (\mathrm{d}^2W/\mathrm{d}S^2)_{\mathrm{eq}} = (\mathrm{d}V/\mathrm{d}S)_{\mathrm{eq}} \tag{2}$$

where we have assumed that $(\mathrm{d}W/\mathrm{d}S)_{\mathrm{eq}} = 0$ and have defined a quantity K_{sym}, the symmetric stretching force constant. To proceed from here, we must now express K_{sym} in terms of experimentally determined bond stretching force constants, and express the potential energy $V(S)$ in terms of an array of point charges in space.

Experimental Value of K_{sym}. Suppose that for a molecule of interest the vibration frequencies have been measured and analyzed in terms of valence-force coordinates;[5] then the vibrational potential function (Born–Oppenheimer electronic energy) is of the form

$$W = (^1/_2)\sum_{i,j} k_{ij}(R_i - R_i^0)(R_j - R_j^0) + \ldots \tag{3}$$

where the k_{ii}'s are bond stretching force constants and the k_{ij}'s are interaction constants. Terms included in eq 3, but not written explicitly, are quadratic bend and bend–stretch interaction terms and cubic and higher order terms. Since $R_i = R_i^0S$ and since the θ_i's are independent of S, inserting eq 3 into the identity in eq 2 yields, for the experimental value of K_{sym}

$$K_{\mathrm{sym}} = \sum_{i,j} k_{ij}R_i^0R_j^0 \tag{4}$$

Note that quadratic bend and bend–stretch interaction terms and cubic and higher order terms do not appear in the expression for K_{sym} in eq 4. Quadratic terms involving angle variables vanish because $\mathrm{d}\theta_i/\mathrm{d}S = 0$. Cubic and higher order terms of all types vanish either because $\mathrm{d}\theta_i/\mathrm{d}S = 0$ or because the second derivatives $(\mathrm{d}^2/\mathrm{d}S^2)$ of these terms contain powers of $(R_i - R_i^0)$ and/or $(\theta_i - \theta_i^0)$ which yield zero when evaluated at equilibrium. Thus, eq 4 is quite general and could be applied to any molecule of arbitrary symmetry and structure, provided the structural data (set of R_i^0) and experimental force constants (all k_{ii} and all k_{ij}) were available.

Since for the present we are interested only in X_2Y_{2n} molecules, eq 4 can be simplified to the form

$$K_{\mathrm{sym}} = k_{\mathrm{XX}}(R_{\mathrm{XX}}^0)^2 + 2nk_{\mathrm{XY}}(R_{\mathrm{XY}}^0)^2 \tag{5}$$

where we have labeled the equilibrium bond length and stretching force constant for the X–X and X–Y bonds as R_{XX}^0 and k_{XX} R_{XY}^0 and k_{XY}, respectively. Cross terms in the potential function have been neglected since they are expected to be relatively small and since they are often not known experimentally. Hence, to this degree of approximation one need only know two bond lengths and two stretching force constants in order to evaluate K_{sym} for a symmetric X_2Y_{2n} molecule.

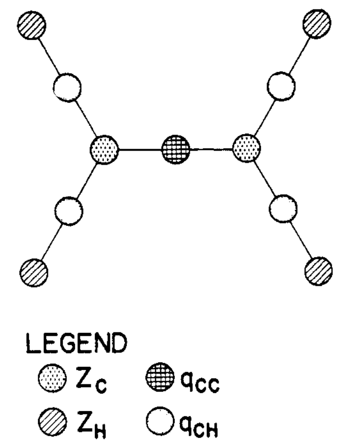

Figure 1. Locations of point charges in the planar C_2H_4 molecule. The charge q_{CC} is located midway between the two Z_{C} charges. Within each C–H bond, the distance from q_{CH} to Z_{C} is $^1/_2R_{\mathrm{CH}}^0S(1 - \alpha)$ and the distance from q_{CH} to Z_{H} is $^1/_2R_{\mathrm{CH}}^0S(1 + \alpha)$, where R_{CH}^0 is the equilibrium C–H bond length, S is the scale parameter, and α varies such that $0 \leq \alpha < 1$.

Bond-Charge Model. The object of this section is to deduce a model expression for the potential energy, V of eq 2, in terms of point charges. The model presented here for X_2Y_{2n} species differs from that given previously for XY_n molecules[8] in one important respect, namely, we now must deal with two different bond charges, a charge $-eq_{\mathrm{XX}}$ representing the valence electrons in the X–X bond and charges $-eq_{\mathrm{XY}}$ representing the valence electrons in each of the equivalent X–Y bonds. (The magnitude of the electronic charge is denoted by e.) The arrangement of point charges in X_2Y_{2n} molecules is therefore as follows: a charge $+eZ_{\mathrm{X}}$ is located at each of the two X nuclei; a charge $+eZ_{\mathrm{Y}}$ is located at each of the $2n$ Y nuclei; a charge $-eq_{\mathrm{XX}}$ is located midway between the two X nuclei; and finally, a charge $-eq_{\mathrm{XY}}$ is located on the line between each of the $2n$ pairs of bonded X and Y nuclei. As an example, the arrangement of charges in the planar ethylene molecule C_2H_4 is shown schematically in Figure 1. In general, for X_2Y_{2n} molecules, symmetry requires that the charge q_{XX} be placed midway between the two X nuclei. However, the charges q_{XY} need not be located midway between their respective X and Y atoms. We only require that the system of q_{XY} charges conform to the molecular symmetry. This latter condition will be satisfied if the locations of all of the q_{XY} charges are controlled by a single parameter α, such that the distance from each q_{XY} to its adjacent X nucleus is $^1/_2R_{\mathrm{XY}}^0S(1 - \alpha)$ and the distance from each q_{XY} to its adjacent Y nucleus is $^1/_2R_{\mathrm{XY}}^0S(1 + \alpha)$, where $0 \leqslant \alpha < 1$, and R_{XY}^0 and S are respectively the equilibrium X–Y bond length and the scale parameter discussed in the previous section. The potential energy can now be written as a sum of all possible Coulomb interactions among the point charges. As an example, we present in eq 6 the expression for the potential energy $V(S)$ for the X_2Y_2 case, as deduced from this scheme.

$$\begin{aligned} V(S) = (e^2/S)\Bigg\{ & \frac{Z_{\mathrm{X}}^2}{R_{\mathrm{XX}}^0} + \frac{2Z_{\mathrm{X}}Z_{\mathrm{Y}}}{R_{\mathrm{XY}}^0} + \frac{2Z_{\mathrm{X}}Z_{\mathrm{Y}}}{R_{\mathrm{XX}}^0 + R_{\mathrm{XY}}^0} + \\ & \frac{Z_{\mathrm{Y}}^2}{R_{\mathrm{XX}}^0 + 2R_{\mathrm{XY}}^0} + \frac{2q_{\mathrm{XX}}q_{\mathrm{XY}}}{(^1/_2)[R_{\mathrm{XX}}^0 + (1 - \alpha)R_{\mathrm{XY}}^0]} + \\ & \frac{q_{\mathrm{XY}}^2}{R_{\mathrm{XX}}^0 + (1 - \alpha)R_{\mathrm{XY}}^0} - \frac{2Z_{\mathrm{Y}}q_{\mathrm{XY}}}{(^1/_2)(1 + \alpha)R_{\mathrm{XY}}^0} - \\ & \frac{2Z_{\mathrm{X}}q_{\mathrm{XY}}}{(^1/_2)(1 - \alpha)R_{\mathrm{XY}}^0} - \frac{2Z_{\mathrm{X}}q_{\mathrm{XX}}}{(^1/_2)R_{\mathrm{XX}}^0} - \\ & \frac{2Z_{\mathrm{X}}q_{\mathrm{XY}}}{(R_{\mathrm{XX}}^0 + (^1/_2)(1 - \alpha)R_{\mathrm{XY}}^0} - \\ & \frac{2Z_{\mathrm{Y}}q_{\mathrm{XY}}}{R_{\mathrm{XX}}^0 + (^1/_2)R_{\mathrm{XY}}^0(3 - \alpha)} - \frac{2Z_{\mathrm{Y}}q_{\mathrm{XX}}}{(^1/_2)R_{\mathrm{XX}}^0 + R_{\mathrm{XY}}^0}\Bigg\} \end{aligned} \tag{6}$$

From eq 6 one sees that the expression for the potential $V(S)$ for an X_2Y_{2n} molecule involves five unknown quantities: Z_X, Z_Y, α, q_{XX}, and q_{XY}. In order to evaluate these five parameters we proceed as follows. First, we make use of the vibrational data contained in K_{sym} by inserting eq 5 into the left-hand side of eq 2 and inserting eq 6 into the right-hand side of eq 2 to give

$$K_{sym} = -e^2F \qquad (7)$$

where, for example, for an X_2Y_2 molecule, F is the expression in braces in eq 6. Second, we note that the overall electrical charge of the molecule or ion will in general be known, and this provides the relationship

$$2Z_X + 2nZ_Y - q_{XX} - 2nq_{XY} = Q \qquad (8)$$

where Q is the molecular charge ($Q = 0$ for a neutral molecule). In order to obtain the three additional equations needed for evaluation of the five unknowns, we appeal to the results of previous work.[7,8] In these papers two schemes were discussed for evaluating the unknown parameters. The first (and simplest) scheme uses a "homopolar" approximation which assumes that the ratio of nuclear point charges is unity, $Z_X/Z_Y = 1$, and that the charge location parameter is $\alpha = 0$, characteristic of an unpolarized bond. Alternatively it was suggested that the ratio of effective nuclear charges can be reasonably approximated by the ratio of Pauling electronegativities χ, *i.e.*, $Z_X/Z_Y \simeq \chi_X/\chi_Y$, and further that the charge location parameter α can be deduced from a "polarization model" which yields $\alpha = (z - 1)/(z + 1)$, where $z = Z_X/Z_Y$.[7] (It may be noted that in the case of ethane, ethylene, and acetylene, with X = C and Y = H, the polarization model yields $z = \chi_C/\chi_H \approx 1.2$ and thus $\alpha \approx 0.1$; *i.e.*, the result is nearly identical with the homopolar model.) The final condition needed to evaluate the complete point-charge system in either the homopolar or polarization models is obtained from our previous[6–8] observation that bond charges are analogous to bond orders. Thus, we suppose that the bond-charge ratio q_{XX}/q_{XY} should be equal to the ratio of bond orders of the X–X and X–Y bonds of a particular molecule, *e.g.*, q_{CC}/q_{CH} = 3.0, 2.0, and 1.0 for acetylene, ethylene, and ethane, respectively. With these assumptions, all of the unknowns can be evaluated.

Formulas for Electric Quadrupole Moments. For a system of discrete point charges, the three components of the electric quadrupole tensor in the principal axis system are given by

$$\begin{aligned} \Theta_{xx} &= (^1/_2)\sum_i e_i(3x_i^2 - r_i^2) \\ \Theta_{yy} &= (^1/_2)\sum_i e_i(3y_i^2 - r_i^2) \qquad (9) \\ \Theta_{zz} &= (^1/_2)\sum_i e_i(3z_i^2 - r_i^2) \end{aligned}$$

where e_i is the magnitude of the charge located at the point (x_i, y_i, z_i), and where $r_i^2 = x_i^2 + y_i^2 + z_i^2$.[4] In the point-charge model for X_2Y_{2n} molecules the quantities e_i are just the set of bond charges $-eq_{XX}$ and $-eq_{XY}$, together with the set of effective nuclear charges eZ_X and eZ_Y. The molecular X–X axis in X_2Y_{2n} is taken to be the x axis. For a linear X_2Y_2 molecule like acetylene we obtain

$$\begin{aligned} \Theta_{xx} = 2S^2e\{&(R_{XX}^0)^2[(^1/_4)Z_X - (^1/_4)q_{XY} + (^1/_4)Z_Y] + \\ &(R_{XY}^0)^2[Z_Y - (^1/_4)q_{XY}(1 - \alpha)^2] + \\ &R_{XX}^0R_{XY}^0[Z_Y - (^1/_2)q_{XY}(1 - \alpha)]\} \qquad (10) \end{aligned}$$

$$\Theta_{yy} = \Theta_{zz} = -(^1/_2)\Theta_{xx} \qquad (11)$$

At the equilibrium geometry, $S = 1$ and the quadrupole moments can be calculated if the bond lengths and the bond and nuclear point charges are known. Formulas analogous to eq 10 can easily be written for other X_2Y_{2n} molecules. Equation 11 is valid for axially symmetric molecules like C_2H_2 and C_2H_6, but not for C_2H_4, where $\Theta_{yy} \neq \Theta_{zz}$.

Results

The input data for our point-charge model calculations on ethane, ethylene, and acetylene are given in Table I. Experimental bond lengths and bond stretching force constants were used in eq 5 to evaluate the symmetric stretching force constants K_{sym}, also given in Table I.

Table I. Structure and Force Constant Data Used to Evaluate the Bond-Charge Parameters for C_2H_{2n} Molecules[a]

Molecule	Bond lengths, Å R_{CC}^0	R_{CH}^0	Bond angles, deg CCH	HCH	Force constants k_{CC}[b]	k_{CH}[b]	K_{sym}[c]
C_2H_2	1.200	1.060	180	180	15.8	5.92	36.06
C_2H_4	1.353	1.071	120	120	9.57	5.08	40.83
C_2H_6	1.534[d]	1.112[d]	109.5	109.5	4.5	4.8	46.20

[a] Experimental data taken from G. Herzberg, "Infrared and Raman Spectra," D. Van Nostrand, New York, N. Y., 1945, except as otherwise noted. [b] Units of millidyne per ångström. [c] Units of erg × 10^{11}. [d] Data taken from L. E. Sutton, Ed., *Chem. Soc., Spec. Publ.*, **No. 11** (1958).

In Table II we present values of the molecular point charges q_{CC}, q_{CH}, Z_C, and Z_H for ethane, ethylene, and acetylene, as deduced from both the homopolar and polarization models. The bond-charge ratios $\gamma = q_{CC}/q_{CH}$ were taken to have the "ideal" bond-order ratios 3.0, 2.0, and 1.0 for acetylene, ethylene, and ethane, respectively. Varying the γ value used in the calculation by ±10% caused a variation of only a few per cent in the computed q and Z values for each molecule. In addition, the data in Table II show that the magnitudes of the calculated charges are not very sensitive to the polarization parameter z, the homopolar

Table II. Calculated Molecular Point Charges for C_2H_{2n} Molecules

Molecule	Model parameters used[a] z	α	γ	Calculated molecular point charges q_{CC}	q_{CH}	Z_C	Z_H
C_2H_2	1.0	0.0	3.0	2.88	0.96	1.20	1.20
	1.2	0.1	3.0	2.82	0.94	1.28	1.07
C_2H_4	1.0	0.0	2.0	2.24	1.13	1.13	1.13
	1.2	0.1	2.0	2.20	1.11	1.25	1.04
C_2H_6	1.0	0.0	1.0	1.23	1.23	1.08	1.08
	1.2	0.1	1.0	1.21	1.21	1.21	1.01

[a] $z = Z_C/Z_H$ = ratio of effective nuclear charges. z = 1.0 for the homopolar model; z = 1.2 for the polarization model. $\alpha = (z - 1)/(z + 1)$ = charge location parameter for locating q_{XY}; see text. $\gamma = q_{XX}/q_{XY}$ = assumed bond-order ratio.

polarization results differing by at most 10%. Hence, the computed charges do not appear to be unduly sensitive to the choice of input parameters.

Values of the *xx* component of the electric quadrupole moments of acetylene, ethylene, and ethane, calculated from eq 9, using the homopolar point-charge data of Table II, were found to be 23.98, 10.51, and 1.93 B, respectively [all values in Buckinghams, B = 10^{-26}(esu cm^2)]. Compared to quadrupole moments from the literature, shown in Table III, the model values are larger by about a factor of 5. However, the relative magnitudes of the quadrupole moments are predicted correctly by our model. To facilitate this comparison of relative quadrupole moment values, we have scaled our calculated values so as to exactly fit Θ_{xx} = 2.0 B for ethylene. These scaled results are presented in Table III and are seen to be in good agreement with available literature values. In addition to the homopolar model calculations given in Table III, we have also calculated quadrupole moments using the polarized bond approximation ("polarization model") described above and earlier.[7,8] These values differed from the homopolar results by less than ± 10%.

Table III. Electric Quadrupole Moments for C_2H_{2n} Molecules[a]

	Scaled point-charge model[b]		Literature	
Molecule	Θ_{xx}	Θ_{yy}[c]	Θ_{xx}	Θ_{yy}[c]
C_2H_2	4.6		3.0[d]	
			5.3[e]	
			3.0–7.0[f]	
C_2H_4	(2.0)	1.0	2.0[d]	
			0.85[e]	1.48[e]
			1.3–4.0[f]	
C_2H_6	0.37		0.1[d]	
			−0.90[e]	
			0.3–1.7[f]	

[a] All values in Buckingham units, B = 10^{-26}(esu cm^2). The C–C bond axis is the *x* axis in every case. [b] Results from the homopolar model, using point-charge values from Table II, scaled to exactly fit Θ_{xx} = 2.0 B for C_2H_4. [c] The quantity Θ_{yy} is trivally related to Θ_{xx}, except in the case of ethylene. In ethylene the *y* axis is chosen to lie in the molecular plane, perpendicular to *x*. [d] Experimental values of A. D. Buckingham, *Quart. Rev., Chem. Soc.*, **13**, 183 (1959); and A. D. Buckingham, R. L. Disch, and D. A. Dunmur, *J. Amer. Chem. Soc.*, **90**, 3104 (1968). [e] Theoretical bond moment values of R. H. Pritchard and C. W. Kern, *ibid.*, **91**, 1631 (1969). [f] Range of other experimental and theoretical values reported in the literature, see ref 4 and the references of footnotes *d* and *e* above.

Discussion of Results

Bond Charges and Bond Orders. The calculated values of the point charges representing valence electrons (q_{CC} and q_{CH} values) and screened nuclei (Z_C and Z_H values) were presented in Table II for both the "homopolar" and "polarization" models. The two sets of results are seen to differ by only a few per cent, which is of negligible importance for the present discussion, so we restrict our attention to results from the simpler, homopolar model.

Previous work has indicated that the magnitude of the bond-charge parameter gives a reasonable empirical measure of bond order,[6–10] and the data in Table II provide further confirmation of this notion. For the carbon–carbon bonds in acetylene, ethylene, and ethane we find values of q_{CC} = 2.9, 2.2, and 1.2, respectively, in agreement with the conventional C–C bond orders of 3.0, 2.0, and 1.0 usually assigned to these molecules. Also the calculated q_{CC} values for C_2H_2 and C_2H_4 agree with the results obtained previously for the corresponding isoelectronic molecules N_2 (q = 2.73) and O_2 (q = 2.26).[6] However, bond charges for the isoelectronic species C_2H_6 (q_{CC} = 1.2) and F_2 (q = 1.8)[6] do not agree very well. The value q_{CC} = 1.2 for ethane seems quite reasonable, but q = 1.8 for fluorine seems too large. The apparent anomaly for fluorine (and halogen compounds in general) has been mentioned previously,[6–8] and Politzer has suggested a modification which eliminates this problem.[10]

The bond-charge values calculated for the C–H bonds in the C_2H_{2n} molecules are also consistent with the identification of bond charges with bond orders. As seen from Table II, the values q_{CH} = 1.0, 1.1, and 1.2 for C–H single bonds in acetylene, ethylene, and ethane are of comparable magnitude to the calculated C–C single bond order of q_{CC} = 1.2 in ethane, but are of considerably smaller magnitude than the calculated C–C double and triple bond orders of q_{CC} = 2.2 and 2.9 for ethylene and acetylene. In addition, the q_{CH} values obtained for the C_2H_{2n} molecules studied here agree well with previously reported C–H bond orders of 1.25 for the diatomic CH molecule[7] and 1.18 for CH_4.[8] Previous work on nominally single-bonded systems comprised of first-row atoms, excluding halogens, has yielded bond orders in the range 0.9–1.3.[6–8] For this reason, we do not attach any important significance to the trend q_{CH} = 1.2, 1.1, 1.0 observed for single bonds in the C_2H_{2n} series.

Electric Quadrupole Moments. The electric quadrupole moments calculated from the bond-charge model for acetylene, ethylene, and ethane (Θ_{xx} = 24.0, 10.5, and 1.9 B, respectively) are substantially larger than corresponding values from the literature, as shown in Table III. This disagreement between literature values and our calculated quadrupole moments is not really surprising. Indeed, we would not expect a crude point-charge model to reproduce subtle molecular electronic structure features such as electric dipole and quadrupole moments with quantitative accuracy. Nonetheless, it is striking to note in Table III the success of the model in predicting the *relative* magnitudes of the quadrupole moments for the series of C_2H_{2n} molecules. The fact that the predicted quadrupole values are too large, but the relative values are given correctly, suggests that the major deficiency of the model lies in exaggerating the extent of charge separation within a molecule. The work of Bader and others[17] has shown that the amount of charge reorganization accompanying molecule formation from atoms is only a small fraction of an electronic charge *e*. Effective nuclear charges on the order of 1.0, as predicted by the present point-charge model, are physically unrealistic. Scaling the calculated quadrupole moments to fit ethylene, as was done in Table III, is equivalent to reducing all of the point charges by a factor of $^{2.00}/_{10.5}$ = 0.19. This scaling is expected to produce a molecular electronic model more

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(17) R. F. W. Bader, W. H. Henneker, and P. E. Cade, *J. Chem. Phys.*, **46**, 3341 (1967); R. F. W. Bader, I. Keaveny, and P. E. Cade, *ibid.*, **47**, 3381 (1967); R. F. W. Bader and A. D. Bandrauk, *ibid.*, **49**, 1653 (1968).

in accord with reality and suffices to give the correct signs and magnitudes for the quadrupole moments in all three C_2H_{2n} molecules.

Acknowledgment. The authors wish to thank the Computer Center at Virginia Military Institute for the use of their facilities.

Perturbation Calculations on the Hydrogen Bonds between Some First-Row Atoms

Jeanne G. C. M. van Duijneveldt-van de Rijdt and Frans B. van Duijneveldt*[1]

Contribution from the Organisch Chemisch Laboratorium,
University of Utrecht, Utrecht, The Netherlands. *Received November 4, 1970*

Abstract: A perturbation theory of intermolecular forces (including exchange) is applied to a hydrogen-bond model system A—H···B. The parameters in the model are chosen to reproduce recent SCF results for some representative systems. Extrapolation then allows H bonds between the first-row atoms C, N, O, F, and Ne to be dealt with. Optimum orientations of the acceptors FH, OH_2, and NH_3 are determined with respect to the A—H···B axis (which is kept linear throughout). Equilibrium H···B distances and H-bond energies are then evaluated for the optimum configurations of these acceptors, as well as for the acceptors F^- and Ne. It is found that major trends in H-bond stability (as measured by $-\Delta H$) can be reproduced reasonably well, although predictions on individual systems are not always reliable. Acceptor strengths are found to diminish in the order N > O > F > Ne, and this is ascribed to the decreasing asymmetry of the lone-pair region in these cases. In practice, F is a better acceptor than our results suggest because of its partial charge which here had to be neglected. The importance of a charge is illustrated by the case of F^-, which is found to form strong H bonds for all donors considered, whereas Ne gives repulsive energies throughout. H bonds involving different proton donors become longer as they get weaker, and in the case of C–H the H···B distance may be too long for the interaction to be classified as an H bond. Analysis of the total interaction energy shows that many of the observed trends in stability can be traced to changes in the electrostatic interaction term alone. This term, however, includes more than the dipole–dipole interaction which has traditionally been considered as the term of primary importance.

As a result of extensive experimental and theoretical work,[2–6] reasonably accurate energies of formation and equilibrium conformations are now available for several hydrogen-bonding systems. In view of the difficulties encountered in accurate experimental work, the most reliable results are probably those yielded by accurate SCF calculations[2] (however, see ref 6c), even though part of the dispersion energy is not obtained in such calculations. Whether we obtain H-bond energies from experiment or from theoretical calculations, the final results in themselves do not tell us where the H-bond stability (as measured by $-\Delta H$) originates from, nor how characteristic differences between different systems should be interpreted. Of course, interpretations tend to be arbitrary, since they are usually based on nonobservable features of the interacting molecules. Nevertheless, they can be useful in organizing the large amount of data available.

With these problems in mind, we present in this paper the results of some semiempirical calculations on a model system A—H···B. Certain concepts such as the polarity of the A–H bond and the hybridization of the lone-pair orbital on B explicitly enter the calculations, thereby allowing an evaluation of their usefulness for interpretative purposes.

Our calculations are based on a perturbation approach[7] in which one calculates the hydrogen-bond energy as the sum of a first-order energy (E^1), comprising a *Coulomb* (or *electrostatic*) term and an *exchange* term, and a second-order energy (E^2), consisting of *induction*, *second-order exchange*, *dispersion*, and *charge-transfer* terms. In principle, exact eigenfunctions for

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(1) Address correspondence to this author.

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