Bond Moments in the Two-Carbon Series Ethane, Ethylene, and Acetylene

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Abstract: Bond dipole and quadrupole electric moments in the C_2 hydrocarbon series ethane, ethylene, and acetylene are examined with *ab initio* wave functions. Net carbon inner-shell, carbon–hydrogen, and carbon–carbon bond moments are defined and evaluated with reference to localized SCF LCAO MO's constructed from minimal basis sets of Slater orbitals. From appropriate combinations of bond moments, the total quadrupole moment for each molecule is rigorously obtained. The sensitivity of the calculated moments to changes in the basis sets is explored for ethane with orthogonalized bond-orbital functions. The results are compared with other bond and molecular moment studies, including those for methane.

Values and trends of the *bond* multipole electric moments in the C_2 hydrocarbons ethane, ethylene, and acetylene have been the subject of widespread interest among chemists for many decades.[2] Although these bond moments have been estimated and related to a variety of chemical effects (*e.g.*, reactive substitution, absorption intensities, barriers to internal rotation), there still seems to be considerable doubt about their magnitudes, and even about the relative sign of the C–H dipole moment, along the series. Part of the uncertainty arises, of course, because the charge distribution for a molecule cannot be resolved uniquely into a sum of localized parts. In general, the use of various localization criteria would be expected to produce different moments for the same fragment, even though the total molecular moment would remain unchanged. Nevertheless, many chemists find it helpful to identify charge densities and electric moments with individual bonds and to relate them to first principles.

Insofar as this is possible, Hartree–Fock theory provides a reasonable starting point because its first-order density matrix produces one-electron moments correct to second order in the correlation error (Brillouin's theorem). Moreover, unitary transformations among the canonical Hartree–Fock molecular orbitals (MO's), which are delocalized over the whole molecule, represent a means of constructing orbitals that are primarily localized between groups of atoms. Lennard-Jones and Pople[3] suggested that a possible quantitative procedure for accomplishing this would be to minimize the interpair MO Coulomb and exchange terms appearing in the expression for the total molecular energy. The use of localized MO's of this type (LMO's) still leaves some arbitrariness in the definition of bond moments in that the nuclear charge needs to be divided among the bonds and local coordinate axes need to be selected. However, the utility of the bond concept suggests that it is still worthwhile to make physically reasonable definitions of net bond moments and to determine their numerical values with *ab initio* LMO's.

In this paper, the dipole and quadrupole bond moments for the hydrocarbon series C_2H_6, C_2H_4, and C_2H_2 are explicitly defined with reference to the approximate Hartree–Fock LMO's that have been constructed recently by Pitzer[4] for C_2H_6 and by Kaldor[5] for C_2H_4 and C_2H_2 from minimal basis sets of Slater orbitals. Since the LMO's for hydrocarbons are readily identified as carbon inner-shell, carbon–hydrogen (C–H), and carbon–carbon (C–C) bond orbitals in which the multiple C–C bond character in C_2H_2 and C_2H_4 is described by equivalent "banana" bonds, it is possible to obtain net moments for each bond and to combine them to form the total moment for the molecule. The results are compared with other bond and molecular moment studies, including those for CH_4.

Localized Bond Moments

To resolve the over-all dipole

$$\boldsymbol{\mu} = e\sum_{K} Z_K \mathbf{R}_K - 2e\sum_{\alpha=1}^{n} \langle \varphi_\alpha | \mathbf{r} | \varphi_\alpha \rangle \qquad (1)$$

and principal quadrupole moments

$$\boldsymbol{\Theta} = \tfrac{1}{2}e\sum_{K} Z_K(3\mathbf{R}_K\mathbf{R}_K - R_K{}^2\mathbf{1}) - e\sum_{\alpha=1}^{n} \langle \varphi_\alpha | 3\mathbf{rr} - r^2\mathbf{1} | \varphi_\alpha \rangle \qquad (2)$$

for a closed-shell molecule described by a single determinant wave function into localized bond contributions $\boldsymbol{\mu}(\alpha)$ and $\boldsymbol{\Theta}(\alpha)$, we associate two units of nuclear charge with each of the n doubly occupied LMO's φ_α and divide this charge equally among the nuclei $\{K\alpha\}$ over which each LMO primarily extends. Choosing the center of charge of each such set $\{K\alpha\}$ of positive charges as the local origin to which the bond moments are defined, we write

$$\boldsymbol{\mu}(\alpha) = -2e\langle \varphi_\alpha | \mathbf{r}_\alpha | \varphi_\alpha \rangle \qquad (3)$$

and

$$\boldsymbol{\Theta}(\alpha) = \tfrac{1}{2}e\sum_{\{K\alpha\}}(3\mathbf{R}_{K\alpha}\mathbf{R}_{K\alpha} - R_{K\alpha}{}^2\mathbf{1}) - e\langle \varphi_\alpha | 3\mathbf{r}_\alpha\mathbf{r}_\alpha - r_\alpha{}^2\mathbf{1} | \varphi_\alpha \rangle \qquad (4)$$

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(2) A review of the early literature is given by W. L. G. Gent, *Quart. Rev.* (London), **2**, 383 (1948).

(3) J. E. Lennard-Jones and J. A. Pople, *Proc. Roy. Soc.* (London), **A202**, 166 (1950).

(4) R. M. Pitzer, *J. Chem. Phys.*, **41**, 2216 (1964).

(5) U. Kaldor, *ibid.*, **46**, 1981 (1967).

where the subscript α on the electron and nuclear coordinate vectors $\mathbf{r}_\alpha$ and $\mathbf{R}_{K\alpha}$ refers them to the local charge center. In the C_2 hydrocarbons considered here, this origin simply occurs either at a carbon nucleus for an inner-shell LMO or at a bond midpoint for the C–H and C–C distributions. Different origins may result for other types of bonds (*e.g.*, three-center bonds). Alternative definitions of $\boldsymbol{\mu}(\alpha)$ and $\boldsymbol{\Theta}(\alpha)$ are also possible, but the present choice enables us to examine the extent to which the bond moments are transferable among molecules and to compare our results with earlier studies in which equivalent conventions were adopted.

The electronic contributions to $\boldsymbol{\mu}(\alpha)$ and $\boldsymbol{\Theta}(\alpha)$ were obtained with LMO's based upon the all-electron, single-determinant SCF wave functions of Palke and Lipscomb[6] for C_2H_2, of Kaldor and Shavitt[7] for C_2H_4, and of Pitzer and Lipscomb[8] for C_2H_6. Minimal basis sets of exponential orbitals with Slater exponents were used, except that a hydrogen exponent $\zeta = 1.2$ was chosen for C_2H_2 and C_2H_4. The wave functions that we employ were constructed at the experimental bond distances and angles. The canonical MO's so obtained were localized by Pitzer[4] for C_2H_6 and by Kaldor[5] for C_2H_2 and C_2H_4 following the iterative procedure of Edmiston and Ruedenberg.[9] It is these LMO's that we identify with the φ_α. All the necessary matrix elements in eq 3 and 4 were evaluated accurately (with errors less than 10^{-5} au) by the Gaussian transform technique.[10]

The results of the computations are given in Tables I and II for the C–H and C–C bonds in the three molecules. The dipole and quadrupole moments are quoted in debyes (10^{-18} esu cm) and in buckinghams (10^{-26} esu cm^2). The x axis points in all cases along the appropriate bond direction with the midpoint taken as origin. The z axes in C_2H_4 and C_2H_6 are perpendicular to the HCC plane that contains the C–H bond of interest. Ethane moments are given for the staggered conformation; the eclipsed values are insignificantly (~1%) different. For C–H bonds, the dipole moment (in the direction C^+H^-) is seen to increase from 1.76 to 1.97 D along the series C_2H_2 to C_2H_6, while the quadrupole component Θ_{xx} along the bond axis decreases from 2.12 to 1.33 B. As expected, the C–H bond quadrupole moments in C_2H_4 and C_2H_6 are not exactly axially symmetric, the asymmetry parameters $|(\Theta_{yy} - \Theta_{zz})/\Theta_{xx}|$ being equal to 0.03 and 0.02, respectively. For the C–C bonds (*cf.* Table II), only quadrupole moments need to be tabulated, since $\boldsymbol{\mu}(\text{C–C}) = 0$ by symmetry. We recall[5] that the multiple C–C bond character of C_2H_2 (or C_2H_4) is described by three (or two) equivalent "banana" bonds. To facilitate comparison with the normal C–C bond moment in C_2H_6, moments for the unsaturated molecules are given for single "bananas," each one of which is spatially oriented to be symmetric on reflection in the xz plane. We note that Θ_{xx} increases from about 3 to 4 B along the series and that large asymmetry factors are present for the banana bonds. The carbon inner-shell moments of $\boldsymbol{\mu}(\alpha)$ and $\boldsymbol{\Theta}(\alpha)$ have also been determined; their values are all negligible compared with the C–H and C–C bond moments. For example, $|\mu_x| \cong 0.003$ D and $|\Theta_{xx}| \leqq 0.03$ B for the C_2 series.

Table I. C–H Bond Dipole and Quadrupole Moments[a]

Moment	C_2H_2	C_2H_4	C_2H_6
$\mu(C^+H^-)$	1.76	1.90	1.97
Θ_{xx}	2.12	1.63	1.33
Θ_{yy}	−1.06	−0.79	−0.68
Θ_{zz}	−1.06	−0.84	−0.65

[a] Dipole $\boldsymbol{\mu}$ and quadrupole $\boldsymbol{\Theta}$ moments are given in debyes and in buckinghams, respectively. The x axis is along the C–H bond direction with the midpoint as origin. For C_2H_4 and C_2H_6, the HCC plane contains the y axis.

Table II. C–C Bond Quadrupole Moments[a]

Component	C_2H_2	C_2H_4	C_2H_6
Θ_{xx}	3.04	3.41	4.09
Θ_{yy}	0.11	−0.45	-2.04_5
Θ_{zz}	−3.15	−2.96	-2.04_5

[a] All results in buckinghams. The x axis is along the C–C bond direction with the midpoint as origin. For C_2H_2 and C_2H_4, values are given for a single "banana" bond spatially oriented to be symmetric on reflection in the xz plane.

The localized C–H, C–C, and inner-shell bond moments can be appropriately combined to yield the molecular moments in Table III. The center of symmetry in the C_2 series ensures that $\boldsymbol{\mu} = 0$, but the molecular quadrupole moments $\boldsymbol{\Theta}$ relative to this origin are nonzero and are subject to experimental measurements. The calculated principal moments Θ_{xx} for C_2H_2 and C_2H_4 are larger in value and opposite in sign to that of C_2H_6 (5.30 and 0.85 B compared to −0.90 B), which has been examined[11] previously with this wave function. The C_2H_2 and C_2H_6 tensors are, of course, axially symmetric while that for C_2H_4 is not. In fact, the C_2H_4 results show that Θ_{yy} and Θ_{zz} are of opposite sign and that their magnitudes are several times Θ_{xx}.

Table III. Molecular Quadrupole Moments[a]

Component	C_2H_2	C_2H_4	C_2H_6
Θ_{xx}(calcd)	5.30	0.85	−0.90[b]
Θ_{yy}(calcd)	−2.65	1.48	0.45[b]
Θ_{zz}(calcd)	−2.65	−2.33	0.45[b]
Θ_{xx}(exptl)	3[c]	+2.0 ± 0.15[d]	−0.8 ± 0.1[d]

[a] All results in buckinghams. The x axis points along the C–C bond and is referred to the center of molecular symmetry as origin. The z axis in C_2H_4 is perpendicular to the molecular plane. [b] Reference 11. [c] References 14 and 15. [d] Reference 12.

Discussion and Comparisons

Before comparing the bond results with previous work, it will be helpful to estimate, within the framework of the theoretical constructs implicit in eq 3 and 4, their probable accuracy. This is not straightforward because individual bond moments are not measurable attributes of a mole-

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(6) W. E. Palke and W. N. Lipscomb, *J. Am. Chem. Soc.*, **88**, 2384 (1966).

(7) U. Kaldor and I. Shavitt, *J. Chem. Phys.*, **48**, 191 (1968).

(8) R. M. Pitzer and W. N. Lipscomb, *ibid.*, **39**, 1995 (1963).

(9) C. Edmiston and K. Ruedenberg, *Rev. Mod. Phys.*, **35**, 457 (1963).

(10) C. W. Kern and M. Karplus, *J. Chem. Phys.*, **43**, 415 (1965).

(11) O. J. Sovers, M. Karplus, and C. W. Kern, *ibid.*, **45**, 3895 (1966).

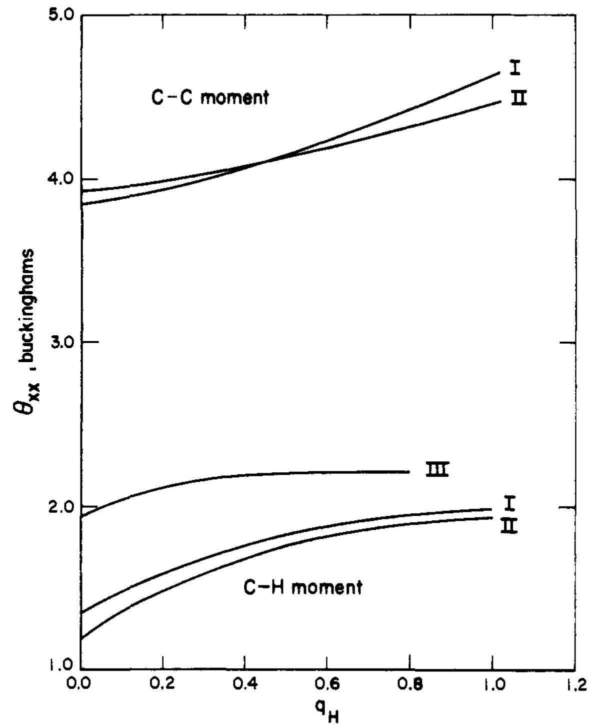

Figure 1. Ethane carbon-hydrogen (C-H) and carbon-carbon (C-C) bond quadrupole components Θ_{xx} *vs.* positive net hydrogen charge q_H for wave functions I, II, and III defined in the text.

cule. On the other hand, molecular quadrupole moments, which can be related to appropriate sums of bond moments, are quantities that can be compared with experiment. Also, variations of the bond moments with changes in the electron density can be useful in assessing the validity of the present LMO results.

Table III shows comparisons between the calculated and experimental data for Θ_{xx}. As reported previously,[11] the ethane moment $\Theta_{xx} = -0.9$ B apparently agrees quite well with the measurements of Buckingham, Disch, and Dunmur[12] which show $\Theta_{xx} = -0.8 \pm 0.1$ B. However, it should be noted[12] that this experimental value may be considerably increased (*e.g.*, $\Theta_{xx} = +0.1 \pm 0.5$ B) when allowance is made for higher polarizability terms. A minimal basis set calculation[11] with orbital exponents optimized for CH_4 does in fact increase Θ_{xx} somewhat to -0.623 B. For C_2H_4, the discrepancy between the theoretical and experimental[12] values is appreciable [Θ_{xx}(calcd) = 0.85 B compared with Θ_{xx}(exptl) = $+2.0 \pm 0.15$ B], although in this case the latter depends on the assumption that the molecular polarizabilities α_{yy} and α_{zz} are equal. For C_2H_2 it seems[13] that the Hartree-Fock value of Θ_{xx} is near 7 B, in which case the best present experimental estimate[14,15] of 3 B may be too low. Refined measurements of Θ_{xx} and calculations with improved wave functions for all three molecules would be very worthwhile.

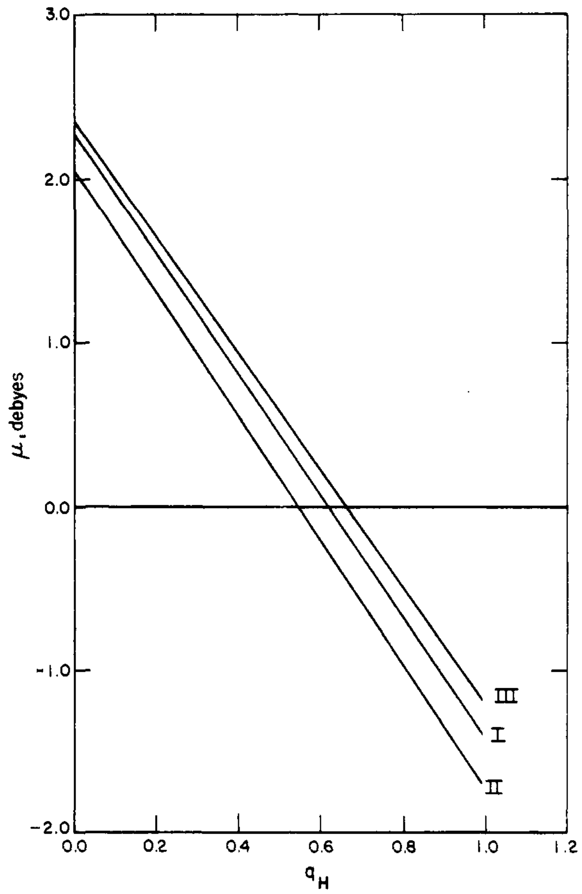

Figure 2. Ethane carbon-hydrogen (C-H) bond dipole moment μ *vs.* positive net hydrogen charge q_H for wave functions I, II, and III defined in the text. A positive μ corresponds to a moment in the direction C^+H^-.

Examining now the sensitivity of the bond moments in Tables I and II to changes in the electron density, let us vary μ and Θ_{xx} with φ_x. For this purpose, we consider the ethane molecule[16] and resort to an all-electron, orthogonalized bond-orbital function that is constructed[11] from a minimal basis set of Slater orbitals and that contains an adjustable parameter which shifts charge, as measured by the net positive charge q_H on each hydrogen atom, along the C-H bond. The value $q_H = 1.0$ corresponds to a wave function in which the coefficients of the hydrogen 1s AO's are equal to zero in all of the nine doubly occupied bond orbitals.

Variation of the orthogonalized bond moments with q_H is plotted for C_2H_6 in Figures 1 and 2 for a basis set of Slater exponents (curves labeled I) and for a set of exponents optimized for CH_4 (curves labeled II). Exponent variation is seen in all cases to be relatively unimportant for fixed q_H. It is known[17] from a total energy calculation with basis set I that the best value of $q_H = 0.06$. Since improved C_2H_6 wave functions probably do not have q_H values much larger than 0.3 (*e.g.*, SCF functions constructed from set I yield[8] $q_H \cong 0.12$), we discuss the range $0 \leq q_H \leq 0.3$. The quadrupole moments (Figure 1) are quite flat in this region: Θ_{xx}(C-C) varies insignificantly

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[12] A. D. Buckingham, R. L. Disch, and D. A. Dunmur, *J. Am. Chem. Soc.*, **90**, 3104 (1968).

[13] A. D. McLean and M. Yoshimine, 1967, quoted by M. Krauss, "Compendium of *Ab Initio* Calculations of Molecular Energies and Properties," NBS Technical Note 438, 1967, p. 68.

[14] Estimated from various sources by A. D. Buckingham, *Quart. Rev.* (London), **13**, 183 (1959).

[15] Krishnaji and V. Prakash, *Rev. Mod. Phys.*, **38**, 690 (1966).

[16] Some C-H bond moment calculations of this type on ethane were performed by O. J. Sovers and C. W. Kern at Columbia University, 1964.

[17] O. J. Sovers, C. W. Kern, R. M. Pitzer, and M. Karplus, *J. Chem. Phys.*, **49**, 2592 (1968).

and $1.3 \leq \Theta_{xx}(\text{C–H}) \leq 1.6$ B. As might be expected, this is not the case for the C–H dipole moment, shown in Figure 2, because the net charge q_H is a good measure of bond polarity and μ(C–H) is seen in fact to be linearly dependent on it. The limits $0.9 \leq \mu(\text{C}^+\text{H}^-) \leq 2.1$ D bounding the reasonable q_H range support the suggestion[18] that $\mu(\text{C}^+\text{H}^-) \geq 0$ in spite of the fact that $q_H \geq 0$ corresponds to a formal charge distribution of C^-H^+. The C–H dipole moment is rather more sensitive than Θ_{xx} to changes in the wave function, but it is unlikely to change sign along the C_2 series, since the net hydrogen charges for all three molecules fall in the same range (0.12–0.16 for SCF functions) of possible q_H values. Such a sign change would either require μ *vs.* q_H plots for C_2H_2 and C_2H_4 that have substantially different slopes from Figure 2 or require a drastic degree of ionicity (*i.e.*, $q_H \geq 0.5$).

The C–H moments in the C_2 hydrocarbons can be compared with those in methane, where LMO's are available for both Slater[19] and optimized[20] minimal basis sets. It is seen from Table I and IV that the C–H bond dipole moment for CH_4 (1.87 D) based upon Slater orbitals ($\zeta = 1.0$) lies between the C_2H_4 ($\zeta = 1.2$) and C_2H_2 ($\zeta = 1.2$) values of 1.90 and 1.76 D, respectively, whereas the corresponding quadrupole moment $\Theta_{xx}(\text{C–H}) = 1.18$ B extends below the C_2H_6 end of the scale for these wave functions. Although we estimate from C_2H_6 bond functions that an increase of the hydrogen ζ from 1.0 to 1.2 changes these moments by only 1%, we see that complete optimization in CH_4, including variation of the carbon exponents, increases both μ and Θ_{xx} by about 10%. Localized MO's of comparable accuracy for the C_2 series are needed to check the unoptimized trends.

Table IV. Effect of Exponent Optimization on the C–H Bond Moments in CH_4[a]

Moment	Slater	Optimized
$\mu(\text{C}^+\text{H}^-)$	1.87	2.02
Θ_{xx}	1.18	1.32
$\Theta_{yy} = \Theta_{zz}$	−0.59	−0.66

[a] Dipole μ and quadrupole Θ moments are given in debyes and buckinghams, respectively.

In any case, the LMO dipole moments for the C–H bond are all substantially larger than Coulson's[18] value of 0.4 D for CH_4, which is typical[21] of other theoretical[22] and experimental[23] estimates. Analysis of Coulson's calculation indicates that these small values of μ occur from the use of a large ratio, equal to 1.8 in the present case, of carbon 2s to 2p orbital exponents. Use of the normal ratio of 1:1 associated with the Slater (and CH_4 optimized) basis sets increases the C–H bond dipole moment by about fivefold. As a consistency check on this conclusion, we note that Coulson's estimated range of μ [1.97 (C^+H^-) to 1.37 D (C^-H^+) in the limits of purely covalent and ionic bonds, respectively] from a valence-bond wave function using normal Slater exponents agrees quite well with the range of μ in Figure 2.

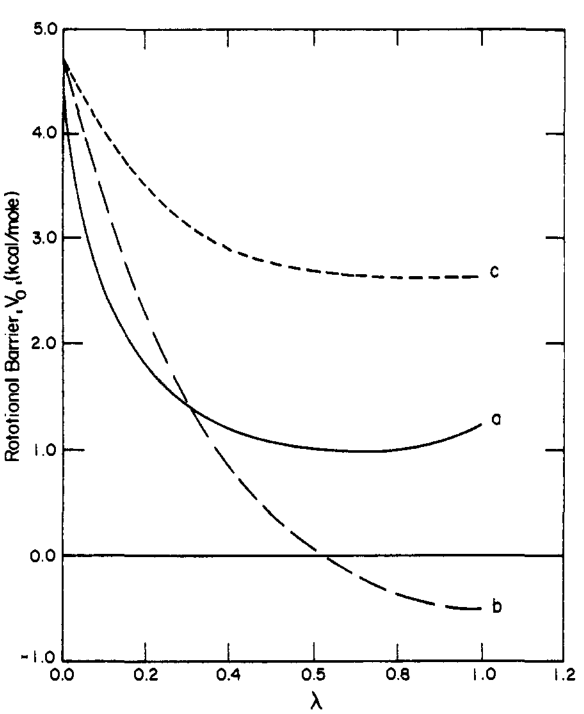

Figure 3. Barrier to internal rotation in C_2H_6 *vs.* C–H bond parameter λ. Curves labeled a, b, and c are identified in the text.

It is of interest to notice in this regard that all of our C–H bond dipole moments can be interpreted as sums of atomic contributions that are only somewhat modified by chemical bonding.[24] Consider, for example, the total dipole moment μ(C–H) of two neutral noninteracting systems of charges composed of a 1s hydrogen atom ($\mu_H = 0$) and of a unit positive charge at carbon with its concomitant electron in an orthogonalized sp^3 hybrid orbital (μ_C). If the quantity $2\mu_C$ is determined by subtracting the proton contribution (−5.3 D) from $\mu(\text{C}^+\text{H}^-) = -1.7$ D at $q_H = 1.0$ on curve II of Figure 2, we have $\mu(\text{C–H}) = \mu_H + \mu_C = +1.8$ D. Since the expected moment $\mu(\text{C}^+\text{H}^-)$ is close to this value, we conclude that, when these two systems are placed in their equilibrium positions and allowed to interact, the resultant charge rearrangement (bonding) alters μ(C–H) to a comparatively small extent. That most previous experimental estimates of the bond dipole yield values which are much smaller than the dominant term representing the intrinsic moment of an sp^3 electron indicates that the moments obtained in these studies cannot be identified with the total bond moment as it is defined in eq 3. Interpretations of the type discussed here can also be made for the C–H bond quadrupole moment.

Bond moments have been discussed by Lassettre and Dean (LD)[25] in the context of electrostatic contributions

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(18) C. A. Coulson, *Trans. Faraday Soc.*, **38**, 433 (1942).

(19) C. Edmiston and K. Ruedenberg, "Quantum Theory of Atoms, Molecules, and the Solid State," Academic Press, New York, N. Y., 1966, p 263.

(20) R. M. Pitzer, *J. Chem. Phys.*, **46**, 4871 (1967).

(21) Exceptions include (a) $\mu(\text{C}^+\text{H}^-) = 2.8$ D by H. Glazer and H. Reiss, *ibid.*, **23**, 937 (1955), from a Thomas–Fermi distribution; (b) $\mu(\text{C}^+\text{H}^-) = 3.9$ D by A. G. Turner, A. F. Saturno, P. Hauk, and R. G. Parr, *ibid.*, **40**, 1919 (1964), from a one-center basis-set expansion; (c) $\mu(\text{C}^+\text{H}^-) = 1.5$ D by R. Moccia, *ibid.*, **40**, 2164 (1964).

(22) For example, see C. R. Mueller and H. Eyring, *ibid.*, **19**, 193 (1951).

(23) For example, see R. E. Hiller and J. W. Straley, *J. Mol. Spectry.*, **5**, 24 (1960).

(24) We thank R. M. Pitzer for pointing this out, and for bringing ref. 21b and the point-charge models discussed there to our attention.

(25) E. N. Lassettre and L. B. Dean, *J. Chem. Phys.*, **17**, 317 (1949).

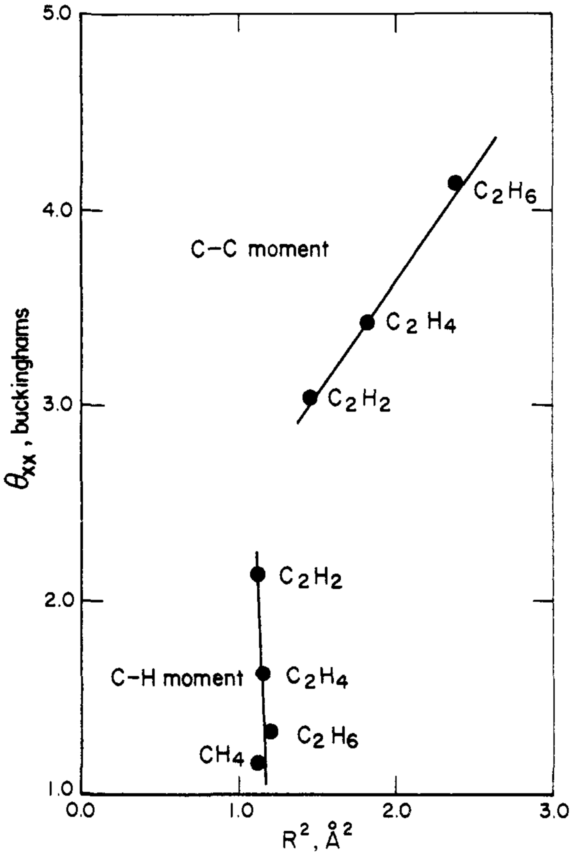

Figure 4. Carbon-hydrogen (C–H) and carbon–carbon (C–C) bond quadrupole moments Θ_{xx} *vs.* the square of the bond length R. Carbon–carbon values refer to single "banana" bonds.

to internal rotation barriers. For ethane, LD used a two-center C–H distribution of the form $\varphi(\text{C–H}) = \chi(\text{C}) + \lambda\chi(\text{H})$, which was assumed to be invariant, except for angular direction, upon internal rotation. The coefficient λ, which can be related to q_H, was varied so as to obtain what was believed to be the correct bond dipole moment (0.4 D in the direction C^+H^-). In Figures 1 and 2, we plot LD's values (curves labeled III) for $\mu(\text{C–H})$ and $\Theta_{xx}(\text{C–H})$ *vs.* q_H. It is seen that in spite of their simple approach, the general range of values is the same as the bond-function results; differences between the two are due in large part to the LD two-center, nonorthogonal distributions, which did not include any admixture of basis functions on other centers.

Table V compares the LMO values of the principal carbon–carbon bond moment along the bond axis with those of LD, which are also based upon a simple two-center wave function. The discrepancies are in opposite directions along the series and differ in magnitude by 25% in the worst case (C_2H_6). The C_2H_2 bond moments are those for only one of the three "banana" bonds, so that it was necessary to divide the LD values by three (or two for C_2H_4).

Table V. Comparison of C–C Bond Quadrupole Moments[a]

Moment	C_2H_2	C_2H_4	C_2H_6
Θ_{xx}(LMO)	3.04	3.41	4.09
Θ_{xx}(LD)	2.85	3.03	5.10

[a] Values (in buckinghams) are based upon single "banana" bonds in the present LMO study and upon two-center distributions in the work of Lassettre and Dean.[25]

We mention parenthetically that LD attempted to describe the barrier to internal rotation in ethane by direct electrostatic interactions between their C–H bond distributions. Their potential function was written in terms of a multipole expansion which was truncated after the quadrupole terms such that the barrier (in kcal/mole) was of the form

$$V_0(\bar{\mu},\bar{\Theta}) = 0.30\bar{\mu}^2 - 0.34\bar{\mu}\bar{\Theta} + 0.31\bar{\Theta}^2 \qquad (5)$$

where $\bar{\mu} = \mu_x(C^+H^-)$ and $\bar{\Theta} = \Theta_{xx}(\text{C–H})$ are expressed in debyes and buckinghams. In Figure 3a, V_0 is plotted as a function of λ for LD's data. This curve can be compared with a recent study by Sovers, Kern, Pitzer, and Karplus[17] in which an infinite-order multipole expansion computed with a bond function similar to LD yielded the V_0 plot in Figure 3b. Clearly, inclusion of higher moments in the LD treatment is needed to obtain convergence of the multipole expansion, especially in the physically significant range of q_H (*i.e.*, $\lambda \cong 0.9$). As is demonstrated by these authors, however, the complete electrostatic barrier potential in Figure 3b diverges significantly from that obtained (Figure 3c) using a properly antisymmetrized bond-orbital wave function which levels off near the experimental value of about 3 kcal/mole.

In Figure 4 the principal quadrupole moment along the bond axis, Θ_{xx}, has been plotted *vs.* R^2, the square of the internuclear distance. A similar plot was given by LD, showing all bond quadrupole moments (C–H, H–H, C–C) to be the same linear function of R^2. Our plot shows this trend to hold only for bonds between the same atoms. From the slopes of the lines and from an examination of the nuclear and electronic contributions involved in eq 4, we find that the net increase in C–C bond moments from C_2H_2 through C_2H_6 is due to the increased C–C bond length, which is only partly balanced by the accompanying spread of electronic charge between the atoms; by contrast, the C–H bond quadrupole moments decrease along this series because electronic contributions increase while the nuclear terms, which depend only upon bond length, remain virtually unchanged.

Tables I–IV contain the dipole and quadrupole moments calculated from the definitions in eq 2–4 with electron distributions based upon all-electron wave functions. Although these functions are only approximate solutions to the Hartree–Fock equations, it seems, in view of the various tests and comparisons that were made, that one may have a reasonable degree of confidence in the results. Nevertheless, it would be useful to compare these minimal basis-set values with moments obtained from extended basis-set LMO's[26] and from alternative localization criteria[27] for the C_2 hydrocarbons and other molecules.

Acknowledgments. We are grateful to Professor R. M. Pitzer for stimulating discussions and to Professor C. A. Coulson and Professor A. D. Buckingham for helpful correspondence.

(26) S. Rothenberg, *J. Chem. Phys.*, in press; G. P. Arrighini, C. Guidotti, M. Maestro, R. Moccia, and O. Salvetti, *ibid.*, **49**, 2224 (1968).

(27) C. Trindle and O. Sinanoglu, *ibid.*, **49**, 65 (1968).