Theoretical Confirmation of the E.S.R. Spectrum of the Ethane Cation

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A C_{2h} structure of the ethane cation, with a 'normal' C–C bond length, has been found as a minimum in the MP2/6-31G** potential energy surface, the isotropic hyperfine coupling constants for this structure, calculated using an accurate configuration interaction method, being in good agreement with the experimental e.s.r. spectral data reported by Iwasaki *et al.*

The ground state of the ethane cation has been an open question, the complexity originating in the electronic structure of the parent molecule, in which the $3a_{1g}$ orbital is very close to the $1e_g$ orbital in energy and the latter level splits into two levels by vibronic coupling when it becomes singly occupied. Experimental evidence[1] indicates that in the case of vertical ionization the ground state of the ethane cation is obtained by ionization from a $1e_g$ orbital. The resulting ^2E_g state is Jahn–Teller unstable, under a diborane-like distortion, leading to a symmetry reduction from D_{3d} to C_{2h}. In the lower symmetry, the ^2E_g state splits into a ^2A_g and a ^2B_g state, of which the former is lower, and the $^2A_{1g}$ state becomes ^2A_g.[2] The configuration interaction (CI) calculations by Richartz *et al.*[2] show that the ground state of the ethane cation is ^2A_g at all C–C distances, with ^2E_g character dominating at short distances and $^2A_{1g}$ character at long distances. The overall minimum of the ^2A_g potential energy curve is obtained at a C–C distance of about 1.85 Å. Essentially the same results were obtained by Bouma *et al.*[3] from their MP2/6-31G* calculations (*i.e.*, calculations using Møller–Plesset perturbation theory[4] terminated at second-order with a 6-31G* basis.[5]) At this C–C distance, the Jahn–Teller distortion has become negligible, so that the symmetry again is D_{3d}.

The e.s.r. spectrum of the ethane cation has been investigated by Iwasaki *et al.* in an SF_6 matrix at 4.2K[6] and it is a 1 : 2 : 1 three-line spectrum with a large splitting of 152.5 G (1G $= 10^{-4}$ T). The authors concluded that radiolytically produced ethane cation exhibits a C_{2h} distortion giving an ^2A_g state and

Table 1. The MP2/6-31G** optimized geometries and total energies, and CI isotropic hyperfine coupling constant values a_H (for notation see Figure 1).

	R/Å	r_1/Å	r_2/Å	α/°	β/°	γ/°	E_{MP2}/E_h	$a_{H,1}$/G	$a_{H,2}$/G
$^2A_g(C_{2h})$	1.579	1.131	1.081	82.6	143.3	115.8	−79.131290	131.3	−8.8
$^2A_{1g}(D_{3d})$	1.918	1.082		98.3			−79.130733	—	—
							Expt[a]	152.5	—

[a] Ref. 6.

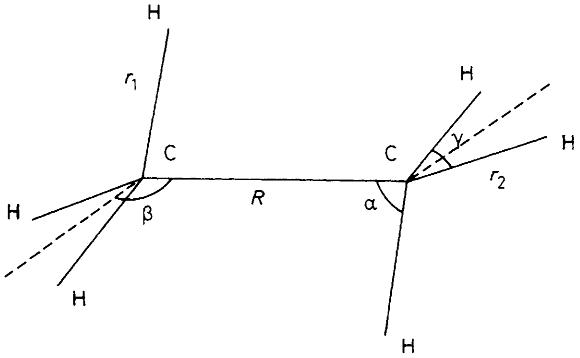

Figure 1. Geometry and labelling used for the ethane cation (C_{2h} symmetry).

that the Me groups tilt inward resulting in the C–C–H bond angle α (see Figure 1) for the in-plane protons being smaller than the tetrahedral angle.

Apparently the experimental results by Iwasaki *et al.* are not compatible with a $^2A_{1g}$ character of the ^2A_g state, but rather with the diborane-like distorted ^2E_g character predicted at shorter C–C distance. However, no minimum at shorter C–C distance in the potential energy surfaces has been found in the previously reported calculations.[2,3] As a possible explanation for this discrepancy, Bellville and Bauld[7] suggested that it is due to the matrix cavity effects, *i.e.*, the molecule is frozen into a conformation with a 'normal' C–C bond length and the anticipated stretching is inhibited by the matrix. It can, however, be noted that neither of the correlated calculations[2,3] included polarization functions on the hydrogen atoms, and such functions were found to be important to stabilize the C_{2v} geometry of the methane cation.[3]

We have therefore performed calculations for the ethane cation to investigate the effects on the ground state geometry, and hence the hyperfine coupling parameters, of using a more accurate basis set including polarization functions on the hydrogens. The results of this Communication will hopefully resolve the existing controversies.

Geometry optimization calculations for the ^2A_g state of the ethane cation were performed using the program GAUSSIAN 86[8] at the MP2 level with a 6-31G** basis.[5] C_{2h} symmetry was imposed and all independent parameters were optimized. Using the MP2/6-31G** optimized geometry of the ^2A_g state, the isotropic hyperfine coupling constants for the hydrogen atoms were obtained from accurate CI calculations, for which the program system MELD[9] was used. For carbon, van Duijneveldt's[10] (13s,8p) basis was used, contracted to [5s,4p] and augmented by a polarization function with exponent 0.75, and for hydrogen his (10s) basis contracted to [4s] and augmented by a polarization function with exponent 1.0. Before CI, the SCF(RHF) virtual orbitals were transformed into K-orbitals.[11] These have been shown to mimic frozen natural orbitals in the cases where the HF configuration dominates the wavefunction, resulting in a more rapidly convergent CI expansion. All single excitations from the ground state HF configuration were included in the CI, as well as the most important double excitations, as selected by second order perturbation theory.[12] The total number of configurations was approximately 30 000, which in the selection of the doubly excited configurations was equivalent to an energy contribution threshold of approximately 4.0 × 10^{-6} E_h. The absolute value of the coefficient of the HF configuration in the final CI wavefunction is 0.9541.

The geometry with the state designation $^2A_g(C_{2h})$, given in the first row of Table 1, was obtained in the full optimization with an initial parameter of 1.628 Å for the C–C bond length, which was shortened to 1.579 Å (see Table 1) upon optimization. This optimized geometry still has C_{2h} symmetry. The optimized values for the angles indicate that the Me groups tilt inward and the α angle is even smaller than 90°. The general features of this geometry indicate that it has a diborane type bridge structure, which is just what Iwasaki *et al.*[6] suggested on the basis of their e.s.r. spectroscopic results. Bouma *et al.*[3] could not find such a structure in their MP2/6-31G* optimization calculations, nor could Richartz *et al.*[2] in their CI calculations, which did not include polarization functions on the hydrogen atoms (though they used bond functions). Therefore we conclude that for predicting such a bridge structure one has to include polarization functions on hydrogen atoms as well as on carbon atoms in the post-SCF calculations.

Our CI calculation for this optimized C_{2h} structure gave the isotropic hyperfine coupling constant values as follows: $a_H(2H) = +131.3$ G for the in-plane protons, and a_H (4H) = −8.8 G for the out-of-plane protons. For the in-plane protons, our CI value 131.3 G is 86% of the experimental value (152.5 G) reported by Iwasaki *et al.*[6] and the agreement is good. Therefore the MP2/6-31G** and CI calculations confirm the e.s.r. spectroscopy experimental results of the ethane cation by Iwasaki *et al.*[6] Our calculated a_H value for the out-of-plane protons is small (−8.8 G), which corresponds to the unresolvable small hyperfine splittings,[6] and it is noted that this value is very close to the experimental value of −9.0 G for the out-of-plane protons in the $MeCD_3$ cation.[6]

With an initial parameter of 1.8 Å for the C–C bond length, the MP2/6-31G** geometry optimization of the ^2A_g state of the ethane cation led to a D_{3d} structure (the state becomes $^2A_{1g}$), which apparently corresponds to the minimum obtained in the previous calculations.[2,3] The geometry parameters for this structure are given in the last row of Table 1. The barrier between the two minima (C_{2h} and D_{3d}) occurs at a C–C distance between 1.628 Å and 1.8 Å in the MP2/6-31G** potential energy surface. The total energy values given in Table 1 indicate that the C_{2h} and D_{3d} structures have almost equal energies, and the former is predicted to be slightly more stable at the MP2/6-31G** level. The CI a_H value for the six equivalent protons in the D_{3d} structure is very small (the absolute value is about 1 G).

Since an energy minimum corresponding to a C_{2h} geometry has been found at a shorter C–C distance, the suggested interpretation[7] that the matrix inhibits the stretching of the C–C bond due to a cavity effect is essentially not needed. However, the matrix may still cause minor corrections to the geometry and the hyperfine coupling constants.

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