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Ab-initio Calculations on Small Hydrides Including Electron Correlation

XI. Equilibrium Geometries and Other Properties of CH_3, CH_3^+, and CH_3^-, and Inversion Barrier of CH_3^-

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The ground state energies of CH_3^+, CH_3, and CH_3^- are calculated both in the SCF (near Hartree-Fock) approximation and in the IEPA-PNO scheme including correlation energy. Due to a more appropriate choice of the basis, our SCF-values for CH_3^- are substantially better than previously published ones. Both CH_3^+ and CH_3 are planar whereas the equilibrium bond angles in CH_3^- are nearly tetrahedral. The inversion barrier of CH_3^- is ~2kcal/mol. The force constants of the out-of-plane bending modes are changed by correlation in the case of CH_3 from 0.03–1.8 mdyn/Å. The localized MO's that correspond to the CH-bonds are "bent" in the non-equilibrium geometries. The dependence of the different pair correlation contributions on the angle γ that describes out-of-plane deformation is analyzed. The electron affinity of CH_3 is ~0.3 eV. Finally the Pariser-Parr disproportionation reaction is analyzed in the light of the present results. Changes in correlation energy for this reaction amount to less than 1 eV.

Key words: Correlation energy – Negative ions – Inversion barrier – Hyperfine coupling constants – Electron affinity

1. Introduction

Many SCF calculations on CH_3^+, CH_3, and CH_3^- have been published so far (for an up-to-date review see [1]), the most refined ones being those of Millié and Berthier [2] and the recent ones [5, 6] of a series of calculations [3–6] by Kari and Csizmadia. To our knowledge quantum chemical treatments of these molecules that take electron correlation into account are virtually non-existing, only a CI calculation of CH_3^- that accounts for about 45% of the estimated correlation energy has to be mentioned [5].

The main concern of the present paper is a study of the correlation energy in CH_3^+, CH_3, and CH_3^- and its influence on the properties of these molecules. We also found, however, that the previous SCF calculations on CH_3^- (not CH_3^+ and CH_3) were performed with inappropriate basis sets. With an improved basis set one not only gets a lower total SCF-energy, but also quite a different inversion barrier.

It is generally accepted that CH_3^+ has a planar equilibrium structure with D_{3h} symmetry, but less definite information has been obtained so far concerning the equilibrium structures of CH_3 and CH_3^-. By analogy with the isoelectronic species NH_3 one should expect a C_{3v} structure for CH_3^- and an inversion barrier of the same order of magnitude, i.e. of a few kcal/mol.

2. The Method

The method used, abbreviated as IEPA-PNO, is the same as in the recent papers in this series (see e. g. [7, 8]). We start from a molecular Hartree-Fock calculation with a basis of gaussian lobes, the doubly occupied orbitals are then transformed to localized ones. For each doubly occupied localized orbital the intrapair correlation energy ε_i and for each pair of orbitals the interpair correlation energy ε_{ij} (a sum of the singlet and triplet contributions ${}^1\varepsilon_{ij}$ and ${}^3\varepsilon_{ij}$) is calculated "in the field of the other electrons". The total correlation energy is approximated as the sum of the different pair contributions. For open shell states like CH_3 the situation is somewhat more complicated, since also correlation contributions involving the singly occupied orbitals have to be included. For details and the general theory the reader is referred to Ref. [9].

3. The Gaussian Basis

For carbon we started from the $10s/6p$ basis of Huzinaga [10] in the contraction [5,1,1,1,1,1] for s and [3,1,1,1] for p and augmented this basis by a set of p-functions[1] with the small exponential factor $\eta = 0.021$ and a set of d-functions with $\eta = 0.65771$. The η-value of the additional p-functions is the result of an energy minimization, whereas variation of the η of the d-functions between 0.5 and 1.0 did not affect the energy much, so for convenience the η-value of the most important p-function was used for the d-functions as well. For hydrogen the $5s$-Huzinaga basis in the contraction [3,1,1] was augmented by a p-set with $\eta = 0.65$.

For the calculation of the correlation energy a second incomplete d-set $(d_{xz}, d_{yz}, d_{z^2})$ on carbon was included with $\eta = 0.2$, this η – value was the result of an optimization of the intrapair correlation energy of the lone pair in CH_3^-. In test calculations the effect of a 8th p-set with $\eta = 0.005$ was found to improve the energy by only 0.0002 a.u., so it was not included, although it had a coefficient of ~ 0.075 in the $1a_2''$ MO.

Our basis set differs from those of previous large calculations [2, 5, 6] mainly in the presence of as many as 5 sets of p groups one of which is very "diffuse" ($\eta = 0.021$). Kari et Csizmadia [5] used 2 sets of p groups, Millié and Berthier [2] 4 sets. It ought to be obvious that for a negative ion diffuse basis functions have to be included. Taking into account that in planar CH_3^- the orbital energy of the highest ($1a_2''$) MO is $\varepsilon = -0.0065$ the appropriate STO for describing its tail behaviour should be [11] $re^{-\alpha r}\cos\delta$ with $\alpha = \sqrt{-2\varepsilon} \approx 0.12$, such an STO has its maximum radial charge density for $r = \dfrac{n}{\alpha} \approx 16a_0$. A gaussian with the maximum at the same distance has $\eta = \dfrac{n}{2r^2} = -\dfrac{\varepsilon}{n} \approx 0.003$. This estimate is, of course, somewhat crude but indicates that unusually small η-values have to be included for negative ions that have orbital energies close to the ionization limit.

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[1] p- and d-functions were constructed from lobes.

4. Discussion of the SCF Results

We calculated the SCF energy of CH_3^- for the planar and different pyramidal configurations (characterized by the angle γ which indicates the simultaneous out-of-plane deformation of the three CH-bonds with respect to a plane perpendicular to the threefold axis) and optimized the CH distance for each value of γ. These equilibrium distances r_e are given in Table 1 together with the orbital energies and the total SCF energy. For $\gamma = 0$ we find $r_e = 2.033\ a_0 \triangleq 1.075$ Å, for $\gamma = 18.5°$ (which corresponds to $\widehat{HCH}$ angles of 110.4°) we find $r_e = 2.069\ a_0 \triangleq 1.095$ Å. This increase in bond length agrees with the picture that in the planar configuration carbon is sp^2- and in the tetrahedral configuration sp^3-hybridized. The lowest energy of CH_3^- is obtained for $\gamma = 18.5°$, and i.e. for practically tetrahedral bond angles. Our SCF energy of -39.51995 a.u. is substantially lower than the claimed "near-Hartree-Fock energy" (-39.51292 a.u. for $\gamma = 23.5°$ and $r = 2.090\ a_0$.) of Ref. [5] or the very similar value (-39.5125 a.u. for $\gamma = 22°$ and $r_e = 2.040\ a_0$.) of Ref. [2]. That the previous results for CH_3^- were unsatisfactory could have been concluded from the orbital energy. In the planar configuration the orbital energy of the lone pair was found positive both in Ref. [5] and [2], whereas we obtain a negative orbital energy[2].

The omission of a set of "diffuse" p-AO's is more serious for the planar configuration than for the equilibrium geometry of CH_3^- (where even the previous calculations gave negative orbital energies for the lone pair), so with a poor basis one gets a spurious destabilization of the planar configuration and too high an inversion barrier. We are therefore confident that our SCF-value of 2.0 kcal/mol for the inversion barrier of CH_3^- is more reliable than the previous values of 5.2 [2] or 5.46 [5] kcal/mol.

Table 1. CH-distances r_e (in a_0), orbital energies and SCF energy of CH_3^- and SCF energies of CH_3 and CH_3^+ as functions of the out-of-plane deformation angle γ

γ	r_e	CH_3^-						CH_3	CH_3^+
		D_{3h}	$1a_1'$	$2a_1'$	e'	$1a_2''$	E_{SCF}	E_{SCF}	E_{SCF}
		C_{3v}	$1a_1$	$2a_1$	e	$3a_1$			
0°	2.033		−10.9642	−0.6466	−0.3196	−0.0065	−39.51675	−39.57055	−39.24471
5°	2.037		−10.9626	−0.6449	−0.3161	−0.0075	−39.51719	−39.57051	
10°	2.044		−10.9573	−0.6413	−0.3069	−0.0107	−39.51841	−39.56965	−39.23173
20°	2.075		−10.9431	−0.6306	−0.2745	−0.0245	−39.51987	−39.55995	−39.19173
30°	2.115		−10.9336	−0.6266	−0.2351	−0.0492	−39.51293		
40°	2.163		−10.9356	−0.6356	−0.1963	−0.0843	−39.48716		

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[2] In fact, (discrete) positive eigenvalues for occupied orbitals of the Hartree-Fock operator of a singly negative ion are perfectly meaningless and can only be an artefact of the chosen basis, irrespective of whether or not the considered state is physically bound. For such ions the potential $V(r)$ in the Fock operator fulfils the condition

$$\lim_{r \to \infty} |r|^{1+\varepsilon} V(r) = 0$$

and this condition is, as Kato [24] has shown, sufficient for the existence of only negative discrete eigenvalues. Positive eigenvalues are hence only possible in a truncated matrix representation and can always be reduced to zero (for continuum states) or below zero (for bound states) by extension of the basis.

Table 2. Coefficient of $r_e^2\gamma^2$ and $r_e^4\gamma^4$ in the expansion of $E(\gamma)$ for CH_3^+, CH_3, CH_3^- with and without correlation (values in a.u.)

Molecule	SCF		With correlation	
	$c(r_e^2\gamma^2)$	$c(r_e^4\gamma^4)$	$c(r_e^2\gamma^2)$	$c(r_e^4\gamma^4)$
CH_3^+	0.1021	−0.0019	0.0930	−0.0046
CH_3	0.0026	0.0336	0.0171	0.0158
CH_3^-	−0.0141	0.0167	−0.0127	0.0172

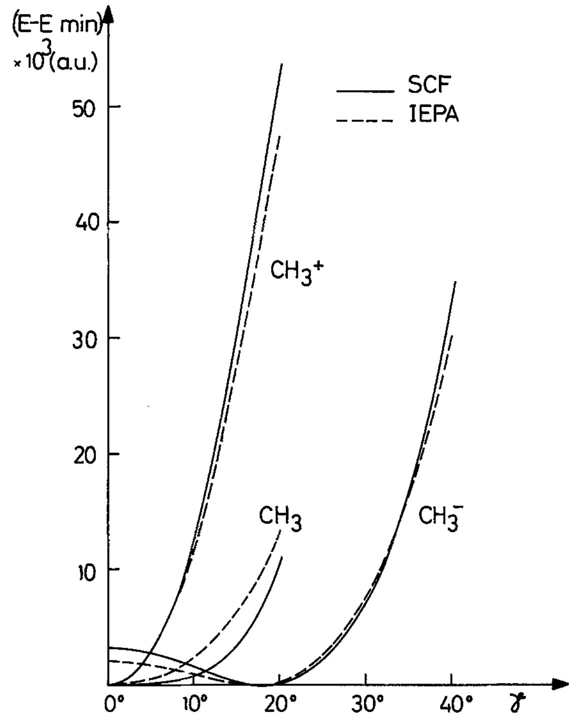

Fig. 1

We performed the SCF calculations for CH_3 and CH_3^+ as functions of γ for those CH-distances r_e that were optimum for CH_3^-. A new optimization of r_e would not have changed the energy appreciably and was not regarded as worthwhile since the absolute minimum of the energy was found for the planar structure both for CH_3 and CH_3^+. We have then optimized the CH-distance only for $\gamma = 0°$ and found $r_e = 2.026\ a_0$ for CH_3 and $r_e = 2.044\ a_0$ for CH_3^+ (compared to 2.033 a_0 for CH_3^-).

Our SCF energies −39.57055 a.u. ($r_e = 2.026\ a_0$) and −39.24471 a.u. ($r_e = 2.044\ a_0$) for CH_3 and CH_3^+ respectively may be compared with −39.57148 a.u. ($r = 2.040\ a_0$) and −39.24592 a.u. ($r = 2.040\ a_0$) of Ref. [2] and −39.57028 a.u. ($r = 2.038$) and −39.24216 a.u. ($r = 2.038\ a_0$) of Ref. [5, 6]. The slightly lower values of Ref. [2] for CH_3 and CH_3^+ (not CH_3^-) are due to the use of two *d*-sets on carbon in Ref. [2].

In Table 2 the coefficients of $r_e^2\gamma^2$ and $r_e^4\gamma^4$ in the expansion of the energy are given. This table confirms what one concludes pictorially from Fig. 1, namely that in SCF-approximation CH_3^+ has a "normal" parabolic dependence on γ, whereas the minimum for CH_3 is extremly flat and practically of the fourth order in γ. The harmonic force constant of CH_3 almost vanishes. In CH_3^-, finally, the coefficient of the γ^2 term is negative and the pyramidal configuration is more stable.

5. The Localized Orbitals in CH_3^+, CH_3, and CH_3^-

We transformed the doubly occupied orbitals of all the molecules to localized ones according to the criterion of Boys [12]. Each localized orbital can be characterized by the distance d of its centroid to the carbon atom and by the angle α that the line connecting the centroid and the atoms forms with a plane perpendicular to the threefold axis. For the localized orbitals corresponding to CH bonds d and α and for the lone orbital just d are given in Table 3 as functions of the bond angle γ.

The angles α do not coincide exactly with the bond angles γ. One may interpret these deviations by saying that the Boys-localized orbitals represent bent bonds. Even if one admits that this may be an artefact of the Boys criterion (which keeps the centroids as far from each other as possible) one realizes that in CH_3^+ and CH_3 the angles α are always smaller than the respective γ's (the molecules want to keep sp^2 hybridized carbon and planar structure), but that α is larger than γ for CH_3^- (the carbon wants to have sp^3 hybridization and tetrahedral arrangement). It is interesting to note that at equilibrium geometry the angles α and γ almost coincide for any of the three molecules. A similar result, though in a slightly different context was found by Klessinger [25] for H_2O. The fact that the localized orbitals do not point towards the H-atoms causes some troubles for CH_3^- in the planar or near-planar configuration. For $\gamma = 0$ we obtain $\alpha = 0$ by the Boys-procedure (unlike to what one finds for OH_3^+ [13]), but the transition from

Table 3. Direction (α) and distance (d in a_0) of the centroids of the localized orbitals referred to the C-atom, for different out-of-plane angles γ

γ	α(CH)			d(CH)			d(lone orbital/ pair)	
	CH_3^+	CH_3	CH_3^-	CH_3^+	CH_3	CH_3^-	CH_3	CH_3^-
0°	0°	0°	0°	1.28	1.38	1.42		0.00
2°			5°			1.42		0.29
5°		4°20′	9°		1.38	1.41	0.18	0.49
10°	7°10′	8°30′	13°50′	1.28	1.39	1.43	0.33	0.66
20°	14°	16°30′	21°40′	1.28	1.40	1.47	0.52	0.84
30°			29°			1.47		0.91
40°			36°20′			1.54		0.88

$\gamma \neq 0$ to $\gamma = 0$ does not seem to be continuous. This has an unpleasant consequence for the calculation of the correlation energy as a function of γ in CH_3^- (but not in CH_3^+ and CH_3).

6. The Correlation Energy and Its Effects

The correlation contributions and their sums are collected in Table 4.

A comparison of the intrapair correlation energy ε_{bb} of a CH-bond and the interpair correlation energy $\varepsilon_{bb'}$ between two CH-bonds in the series CH_3^+, CH_3, and CH_3^- shows nicely the effect of the different "availability" of the p_z-AO of carbon for correlation. In CH_3^+ where this AO is "fully available" $|\varepsilon_{bb}|$ and $|\varepsilon_{bb'}|$ are larger than in CH_3 and in CH_3^-. Both $|\varepsilon_{bb}|$ and $|\varepsilon_{bb'}|$ increase with γ, for $|\varepsilon_{bb'}|$ this increase is due to the fact that in the pyramidal structure the CH-bonds get closer to each other.

The total correlation energy for CH_3^+ (to which only ε_{bb} and $\varepsilon_{bb'}$, contribute) increases therefore in absolute value with γ, it lowers the energy more for large than for small γ, i.e. it makes the potential curve of Fig. 1 somewhat flatter. Inclusion of correlation reduces the out-of-plane force constant of CH_3^+ somewhat (see Table 5). A similar effect has been found for the isoelectronic molecule BH_3 [8].

In neutral CH_3 the contributions to the correlation energy that involve the singly occupied "lone" orbital (ε_{bn}) decrease in absolute value with increasing γ. This decrease overcompensates the increase of $|\varepsilon_{bb}|$ and $|\varepsilon_{bb'}|$, so that the $|E_{\text{corr}}|$ of CH_3 decreases with γ. The decrease of $|\varepsilon_{bn}|$ with γ is understandable because the more the molecule is bent the more is the lone orbital localized and distant from the CH-bonds.

In CH_3 inclusion of correlation makes the potential curve of Fig. 1 somewhat steeper (unlike in CH_3^+). The harmonic out-of-plane force constant of CH_3 which was only 0.034 mdyn/Å in the SCF approximation becomes 0.175 mdyn/Å when correlation is taken into account. Experimental values of 0.159 mdyn/Å (gaseous CH_3 [18]) and 0.253 mdyn/Å (in argon matrix [14]) have been reported, neither of which is "harmonic", i.e. corrected for unharmonicity effects. Our computed force constant should rather be compared to the first value. In view of the experimental difficulties and the (computed) high anharmonicity of the potential one cannot say whether either the experimental or the theoretical value is most reliable. Millié and Berthier [2] have already pointed out that the computed value of this force constant is highly sensitive to changes in the basis, they found 0.175 mdyn/Å in an SCF calculation without polarization functions (*d* on C and *p* on H) and 0.014 when they include polarization functions. Inclusion of polarization functions and of correlation have an opposite effect on this force constant.

As to the correlation energy of CH_3^- and its dependence on the out-of-plane angle γ the situation is somewhat less straightforward. The sum of the intra- and inter-pair contributions of the CH-bonds is very close to the respective one for CH_3, except for $\gamma = 0°$ where (as we already mentioned in Section 5) the result of the Boys-localization seems to depend discontinuously on γ. Similarly the intrapair correlation energy ε_{nn} of the lone pair decreases in absolute value with decreasing angle, but jumps when coming to $\gamma = 0°$. We have therefore decided to extrapolate the values for $\gamma \geqq 10°$ to $\gamma = 0°$ and to take the extrapolated

Table 4. Correlation energy contributions and their sums for CH_3^+, CH_3, CH_3^- as function of the out-of-plane γ

CH_3^+

	0°/2.033	10°/2.044	20°/2.075
$-\varepsilon_{bb}$	0.03238	0.03254	0.03316
$-{}^1\varepsilon_{bb'}$	0.00739	0.00750	0.00786
$-{}^3\varepsilon_{bb'}$	0.00966	0.00979	0.01024
E_{corr}	0.14829	0.14949	0.15378

CH_3

	0°/2.033	5°/2.037	10°/2.044	20°/2.075
$-\varepsilon_{bb}$	0.02964	0.02966	0.02973	0.02995
$-{}^1\varepsilon_{bb'}$	0.00531	0.00534	0.00543	0.00575
$-{}^3\varepsilon_{bb'}$	0.00886	0.00889	0.00900	0.00945
Sum of CH-bond contributions	0.13143	0.13167	0.13248	0.13545
$-{}^1\varepsilon_{bn}$	0.00891	0.00875	0.00836	0.00752
$-{}^3\varepsilon_{bn}$	0.00861	0.00851	0.00830	0.00776
Sum of CH-bond-lone electron interaction	0.05256	0.05178	0.04998	0.04584
E_{corr}	0.18399	0.18345	0.18246	0.18129

CH_3^-

	(calc.)		(extrap.)	(calc.)			
	[0°/2.033]	[5°/2.037][a]	0°/2.033	10°/2.044	20°/2.075	30°/2.115	40°/2.163
$-\varepsilon_{bb}$	0.02916	0.02915		0.02930	0.02969	0.02989	0.02978
$-{}^1\varepsilon_{bb'}$	0.00517	0.00559		0.00582	0.00604	0.00634	0.00707
$-{}^3\varepsilon_{bb'}$	0.00854	0.00912		0.00951	0.01014	0.01085	0.01198
Sum of CH-bond contributions	0.12861	0.13158	0.1328	0.13389	0.13761	0.14124	0.14649
$-{}^1\varepsilon_{bn}$	0.01183	0.01093		0.01037	0.00957	0.00909	0.00898
$-{}^3\varepsilon_{bn}$	0.01727	0.01620		0.01575	0.01491	0.01394	0.01327
Sum of CH-bond-lone pair interaction	0.08730	0.08139	0.0806	0.07836	0.07344	0.06909	0.06675
$-\varepsilon_{nn}$	0.02850	0.02640	0.0264	0.02711	0.02764	0.02786	0.02812
E_{corr}	0.24441	0.23937	0.2398	0.23936	0.23869	0.23819	0.24136

[a] Due to the localization discontinuity (see Section 6) even the values for 5°/2.037 are unreliable.

correlation energy as reference for the discussion of the γ-dependence of E_{corr} in CH_3^-. With this correction we get the potential curves in Fig. 1 and the force constants in Table 5. The extrapolation procedure is not very accurate and may be in error by as much as 1 kcal/mol. We therefore do not put much stress on the change of the inversion barrier from 2 kcal/mol in SCF approximation to

Table 5. Force constants (in mdyn/Å) for the out-of-plane bending vibration

	CH_3^+	CH_3	CH_3^-
SCF	1.06	0.034	0.265
With correlation	0.96	0.175	0.235
exp.	—	0.159 [18] 0.253 [14]	—

1.5 kcal/mol with correlation. We rather think that for CH_3^- the total correlation is – within the limits of the method – invariant with respect to changes of γ, and that, therefore, the SCF value for the barrier is a good approximation to the true one. This statement cannot be checked for CH_3^-, because an experimental barrier is not known, but the analogous claim for the isoelectronic NH_3 [15] is generally accepted.

The extrapolation problem is irrelevant for the CH_3^- near its equilibrium geometry. Inclusion of correlation changes the optimum γ slightly to 18° (corresponding to a HCH angle of 111°) where the total energy is -39.7588 a.u.

From the experience with similar basis sets for comparable molecules we can assume that we have accounted for about 90% of the valence shell correlation energy. By extrapolating to 100% and adding the estimates (0.057 in CH_3^+, 0.059 in CH_3, 0.061 in CH_3^-)[3] for the contributions involving the K-shell of carbon we get the following estimated (absolute values of the) correlation energies in the equilibrium geometries:

$$CH_3^+ \ 0.220 \text{ a.u.}, \quad CH_3 \ 0.262 \text{ a.u.}, \quad CH_3^- \ 0.325 \text{ a.u.}$$

7. Binding Energy, Ionization Potential and Electron Affinity of CH_3

The computed total energy of CH_3 is -39.7545 a.u. If we substract the energy of the carbon ground state (^3P) calculated with a comparable basis [16] of -37.7783 a.u. and of three H-atoms ($3 \times 0.49986 = 1.49958$) we get the binding energy

$$\Delta E_e = -0.4767 \text{ a.u.} \approx 300 \text{ kcal/mol}.$$

If we correct for the zero-point energy of $-6000 \text{ cm}^{-1} \approx 17$ kcal/mol we get $\Delta E \approx 283$ kcal/mol which may be compared with the "recommended" experimental binding energy of CH_3 of 291 kcal/mol [17].

The difference of the total energies (including correlation) of CH_3 (-39.7545 a.u.) and CH_3^+ (-39.3930 a.u.), namely 0.3615 a.u. $\triangleq 9.83$ eV gives us the vertical ionization potential. In SCF approximation we find 8.86 eV, whereas the experimental ionization potential is 9.84 eV [18] in agreement with the calculated value including correlation. The Koopmans theorem gives 10.3 eV.

We obtain the (adiabatic) electron affinity A of CH_3 as the difference between the total energies of CH_3 (-39.7545 a.u.) and CH_3^- (-39.7586 a.u.). While in SCF

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[3] 0.045 for ε_{KK} and 0.004 for any ε_{Kb}.

approximation CH_3^- is not stable with respect to CH_3 ($A = -1.38$ eV) our calculation that include correlation gives $A = 0.11$ eV for the adiabatic electron affinity. If we use the estimated correlation energies given at the end of Section 5 rather than the computed ones we get $A = 0.33$ eV[4]. So we conclude that the correct electron affinity of CH_3 is 0.3 ± 0.1 eV. We think that this value is more reliable than the experimental one of 1.1 eV [19]. The experiment on which it is based (magnetron techniques) is so complicated and so subject to errors that it may easily be wrong by 1 eV or more.

8. The Pariser-Parr "Disproportionation Reaction" and the Correlation Energy of a Doubly Occupied π-AO

In the semiempirical π-electron theory the so-called Pariser-Parr disproportionation reaction [20] played a central role. Let us formulate it for CH_3 rather than for C in the $tr^3\pi$ valence state. The exact reaction energy of the hypothetic reaction

$$2CH_3 \rightarrow CH_3^+ + CH_3^-$$

(keeping all three molecules in the same, planar geometry) is, of course, equal to the difference between vertical ionization potential I and electron affinity A of CH_3 (the vertical and adiabatic A of CH_3 differ by only 2 kcal/mol $\sim$ 0.1 eV, namely by the inversion barrier). We have therefore

$$\Delta E = I - A_{\mathrm{ad}} = 9.8 \text{ eV} - 0.2 \text{ eV} = 9.6 \text{ eV}.$$

In the Hartree-Fock approximation one gets

$$\Delta E_{\mathrm{HF}} = I_{\mathrm{HF}} - A_{\mathrm{ad,HF}} = 8.9 \text{ eV} + 1.4 = 10.3 \text{ eV}.$$

The correlation contribution to this disproportionation is hence roughly 0.7 eV.

Let us now assume tentatively that the occupied MO's in CH_3^+, CH_3, and CH_3^- are the same and equal to the correct ones for CH_3. We have calculated the energies of both CH_3^+ and CH_3^- in the planar configuration with the MO's of CH_3. The "non-relaxed" Hartree-Fock energies of CH_3^+ and CH_3^- are respectively 1.3 and 2.7 eV. above the correct Hartree-Fock energies, which leads to

$$\Delta E_{\mathrm{nonrelaxed}} = I_{\mathrm{n.r.}} - A_{\mathrm{n.r.}} = 10.2 \text{ eV} + 4.1 \text{ eV} = 14.3 \text{ eV}.$$

On the other hand this "reaction energy" of 14.3 eV is equal to the self-repulsive energy

$$(\pi\pi|\pi\pi) = 14.3 \text{ eV}$$

of the lone π-orbital in CH_3^-. The crudest possible approach to ΔE would consist in approximating this π-MO by a simple STO according to Slater's rules. It is well known [20] that one then gets $\sim$ 17 eV for $(\pi\pi|\pi\pi)$ and hence for ΔE. In analyzing the different contributions that reduce ΔE from $\sim$ 17 to eventually $\sim$ 10 eV (for a discussion of previous work on this topic see [21]) one realizes that a reduction by $\sim$ 3 eV is achieved if one replaces the $2pz$-STO by the Hartree-

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[4] The analogous correction would only have a small influence on ΔE_e (= 287 kcal/mol) and I (10.0 eV).

Fock AO of CH_3. An additional reduction by 4 eV is obtained if one allows for a relaxation of the orbitals from CH_3 to the ions, mainly for a change of the π-AO from CH_3 to CH_3^-. The final decrease by 0.7 eV due to inclusion of correlation is almost negligible. This is in strong contrast to Pariser and Parr's original hypothesis that the reduction of the $(\pi\pi|\pi\pi)$ integral from $\sim$ 17 to $\sim$ 10 eV is mainly a correlation effect.

Nevertheless we also like to know which pair correlation energies are responsible for these $\sim$ 0.7 eV of change in correlation energy. We first note that the only new term in $CH_3^+ + CH_3^-$ compared to 2 CH_3 is the intrapair correlation energy of the lone (π-)pair ε_{nn} in CH_3^-. This was calculated to be $\sim$ 0.026 a.u. $\triangleq$ 0.7 eV, so it is actually equal to the difference in correlation energy. A more careful analysis shows, however, that the other contributions (which are present for all three or two of the species) change as well and that it is rather accidental that the change in correlation energy equals one particular (new) pair contribution.

9. Spin Densities and Hyperfine Coupling Constants in CH_3

CH_3 is the simplest π-radical and has as such vanishing spin density in restricted-Hartree-Fock approximation both at the C and the H nuclei. A wavefunction like ours that accounts for the intergroup correlation between the lone orbital and the CH-bonds should also be able to furnish good spin densities. Rather than to compute the spin density from the complete wavefunction we have only calculated the bulk contribution to it, the so-called spin-polarization terms which are the only ones linear in the expansion coefficients of substituted configurations. Let the restricted HF-wavefunction be

$$\varphi = |b_1\bar{b}_1 b_2\bar{b}_2 b_3\bar{b}_3 n|\,,$$

then one of the three equivalent spin polarization configurations is

$$\psi_{sp}^{(1)} = \frac{1}{\sqrt{6}}\{-|b_1\bar{p}_1 b_2\bar{b}_2 b_3\bar{b}_3 n| + |p_1\bar{b}_1 b_2\bar{b}_2 b_3\bar{b}_3 n| + 2|b_1 p_1 b_2\bar{b}_2 b_3\bar{b}_3\bar{n}|\}$$

with the spin-polarization orbital p_1 determined such that it minimizes the energy of the two-configuration function

$$\Psi = c_0\varphi + c_1\psi_{sp}^{(1)}\,.$$

The spin density

$$\varrho(\boldsymbol{R}) = \frac{1}{M_s}\int \psi^* \sum_k 2S_{Z_k}\delta(\boldsymbol{R} - \boldsymbol{r}_k)\psi\, d\tau$$

is then first order in c_1 given by

$$\varrho(\boldsymbol{R}) = \frac{1}{M_s}\left\{c_0^2|n(\boldsymbol{R})|^2 + \frac{4}{\sqrt{6}}\sum_{i=1}^{3} c_0 c_i p_i(R) b_i(R)\right\}.$$

With the values

$$\begin{array}{llll} c_0 & = 0.959 & c_1 & = -0.0574 \\ b_1(\boldsymbol{R}_{\mathrm{H1}}) & = 0.4573 & p_1(\boldsymbol{R}_{\mathrm{H1}}) & = 0.4296 \\ b_1(\boldsymbol{R}_{\mathrm{H2}}) & = -0.0338 & p_1(\boldsymbol{R}_{\mathrm{H2}}) & = 0.1622 \\ b_1(\boldsymbol{R}_{\mathrm{C}}) & = -0.5778 & p_1(\boldsymbol{R}_{\mathrm{C}}) & = 0.8299 \end{array}$$

we get

$$\varrho(\boldsymbol{R}_{\mathrm{C}}) = 0.259$$

$$\varrho(\boldsymbol{R}_{\mathrm{H}}) = -0.035$$

and the hyperfine coupling constants

$$\frac{a}{h} = \frac{4\pi}{3h} g g_{\mathrm{N}} \beta \beta_{\mathrm{N}} \varrho(\boldsymbol{R}_{\mathrm{N}})$$

$$a(\mathrm{C}) = 145.4\,\mathrm{MHz} = 52\,\mathrm{Gauss}\,,$$

$$a(\mathrm{H}) = -74.5\,\mathrm{MHz} = -26.6\,\mathrm{Gauss}\,.$$

The experimental values are 41 and −23 Gauss, respectively [23].

Perfect agreement with experiment cannot be expected for several reasons.

1. With gaussian basis functions the values of the wavefunction at the nuclei are somewhat too small. This can be corrected with a trick proposed by Meyer [22] which we have not used.
2. Other terms than the spin-polarization function contribute to the spin density as well, though probably to much less extent.
3. The experimental coupling constants are averages over the zero-point vibrations. For the out-of-plane bending mode large amplitudes are expected and for pyramidal arrangement the restricted Hartree-Fock value is different from zero.

We postpone a comparison with previous theoretical values [22, 26, 27] to a forthcoming paper, where we study these additional effects in detail.

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