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Intermolecular interactions involving C-H bonds. 3. Structure and energetics of the interaction between CH_4 and CN^-.

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Abstracts

On the basis of SCF and single reference MP2 calculations, the full potential energy surface of the interaction between CH_4 and CN^- was studied using extended basis sets of up to near Hartree-Fock limit quality. Colinear arrangements $C\text{-}N^{-}\cdots H\text{-}CH_3$ and $N\text{-}C^{-}\cdots H\text{-}CH_3$ are found to be the only two energy minima. The binding energies of these two structures are calculated to be 2.5 and 2.1 kcal/mol, respectively, at the MP2 level. The full vibrational analyses of the two structures show a red shift of about 30 cm^{-1} for the ν_s C-H stretching.

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Introduction

In the present work, we examine the interaction between CN^- and CH_4 on the basis of ab initio calculations to evaluate the nature and magnitude of the C-N$^-$···H-CH_3 and N-C$^-$···H-CH_3 contact interactions. Since a C-H bond is less polar than F-H and O-H bonds, the C-N$^-$···H-CH_3 and N-C$^-$···H-CH_3 interactions are expected to be weaker than the C-N$^-$···H-F and C-N$^-$···H-OH interactions recently studied by Lee [1]. Our calculations on C-N$^-$···H-CH_3 and N-C$^-$···H-CH_3 could provide relevant information on the nature and strength of the interactions that C-H bonds of organic donor molecules make with counter anions containing CN^- groups in organic donor salts (e.g., C-N$^-$···H-C and N-C$^-$···H-C contact interactions) [2]. No experimental data are available for the energetics of the C-N$^-$···H-C and N-C$^-$···H-C contact interactions in organic salts. So far, neither computational nor experimental studies have been carried out on the CN^-···methane complex.

In our study of the CN^-···methane complex, we perform SCF and single reference MP2 calculations to determine its potential energy surface. Since the HOMO-LUMO separations in the CN^- and CH_4 fragments are large, single reference MP2 calculations are expected to give a good description of the CN^-···methane complex. In addition, according to the binding energy calculations of the CN^-···HF and CN^-···H_2O complexes using a triple zeta plus double polarization plus diffuse s and p basis set [1], both the SCF and single reference MP2 methods give results in good agreement with those obtained from singles and doubles CI as well as singles and doubles coupled cluster calculations. Therefore, the present SCF and single reference MP2

calculations are expected to provide reliable estimates of the binding energy of the CN^-···methane complex.

Computational details

To study the potential energy surface of the CN^-···methane complex, we perform calculations on the three geometrical arrangements shown in **1-3**. The C-N^-···H-CH_3 (**1**) and and N-C^-···H-CH_3 (**2**) arrangements are models for studying the C-N^-···H-C and N-C^-···H-C contact interactions, respectively. The CN^-···methane arrangement **3** is used to examine the energetics associated with the C-H···anion contact change from **1** to **2**.

In order to accurately describe anionic systems, use of large enough basis sets with diffuse functions are needed [3]. At the same time, a precise description of intermolecular interactions requires the use of at least double zeta plus double polarization basis sets [4]. One basis set satisfying both requeriments is the 6-31++G(2d,2p) basis implemented in GAUSSIAN-86 [5]. Use of this basis set and the MP2 method for the potential energy surface calculations is too demanding computationally, so that we carried out the potential energy calculations with the standard 6-31++G(d,p) basis set at the SCF level. After identifying the characteristics of the surface, precise calculations, including reoptimization of the geometry, were performed with more extended basis sets at the single reference MP2 level on some regions of the potential energy surface. All computations were carried out with the GAUSSIAN-86 program [5].

Results and discussion

1) Potential energy surface of the CN^-···methane interaction

For the CN^-···HF and CN^-···H_2O complexes, the SCF method gives geometries and binding energies very close to those obtained with the MP2 method [1]. It is noted that the SCF results in Ref. 1 are closer to experiment and are within 1 kcal/mol of the experimental values. Therefore, we expect to obtain a reasonable picture of the nature of the CN^-···methane interaction by carrying out SCF calculations with the 6-31++G(d,p) basis set. The potential energy surface for **1-3**, obtained as a function of the two parameters defining the interaction between the frozen fragments [6], is shown in Figure 1. This surface is characterized by two minima and a transition state linking them: one minimum is found for the CN^-···H-CH_3 arrangement (**1**) at r_{NH} = 2.652 Å and $\theta = 0°$, another minimum corresponds to the NC^-···H-CH_3 arrangement (**2**) at r'_{CH} = 2.975 Å and $\theta = 0°$, and the transition state lies in the vicinity of the nitrogen atom (i.e., in terms of Diagram **1**, it is located at $r_{NH} \approx 3$ Å and $\theta \approx 90°$). The binding energy for the colinear CN^-···H-CH_3 arrangement(**1**) is calculated to be 1.77 kcal/mol before correcting the basis set supperposition error (BSSE) [4,7], and 1.69 kcal/mol once the BSSE is corrected using the full counterpoise method [8]. The binding energy for the colinear NC^-···H-CH_3 arrangement (**2**) is calculated to be 1.44 kcal/mol before the BSSE correction, and 1.24 kcal/mol with the BSSE corrected. The transition state was accurately located on the potential

energy surface by carrying out analytical second derivatives calculations with the 6-31++G(d,p) basis set at the SCF level. This search locates the transition state at r_{NH} = 3.030 Å and θ = 76.76° in terms of Diagram **1**. The transition state is primarily described as a variation on the angle θ. The hessian matrix has one very small negative eigenvalue (-0.0016) in agreement with the very flat potential energy surface near the transition state. The transition state is 0.7 kcal/mol higher in energy than the optimum $CN^-\cdots H\text{-}CH_3$ arrangement (**1**), and 0.4 kcal/mol higher than the optimum $NC^-\cdots H\text{-}CH_3$ arrangement (**2**). Thus, the $CN^-\cdots$methane complex is weakly bound with two colinear minimum energy arrangements. Its binding energy is much smaller than those of the $CN^-\cdots HF$ and $CN^-\cdots H_2O$ complexes (the experimental values are 21.1 and 12.7 kcal/mol, respectively [9]). The potential energy surface is very close to spherical and very flat in the vicinities of the colinear minima.

The effect of correlation energy on the SCF potential energy surface has been studied at the MP2 level using the 6-31++G(d,p) basis set. Figure 2a shows the variation of the energy of the colinear arrangement **1** as a function of r_{NH} at the SCF and MP2 levels, and Figure 2b that calculated as a function of the angle θ (with the r_{NH} distance fixed at the optimum MP2 value of 2.489 Å). Figure 2 shows that the inclusion of correlation energy, which accounts for the dispersion component of the interaction energy, increases the interaction energy: the binding energy changes from 1.77 kcal/mol at the SCF level to 2.54 kcal/mol at the MP2 level (which become 1.69 and 2.07 kcal/mol, respectively, once the BSSE is corrected). Furthermore, the MP2 energy depends less on the angular variations than does the SCF energy. Though not shown, similar results are found for **2**.

To show that our findings obtained using the frozen fragment geometries remain valid when the geometries are relaxed, we performed a full optimization of the geometry of the complex **1** at the SCF and MP2 levels with the 6-31++G(d,p) and 6-31++G(2d,2p) basis sets. Table 1 lists the optimized geometrical parameters and the total energies of the $NC^-\cdots H\text{-}CH_3$ arrangement (**1**) and its fragments. Table 2 gives similar results for the $CN^-\cdots H\text{-}CH_3$ arrangement (**2**). It is clear from Table 1 and 2 that the geometries and binding energies are not strongly affected either by the geometry relaxation or by the basis set employed. However, at the MP2 level, both minima have shorter interfragment distances and become more stable. Therefore, use of frozen fragments seems to be a good starting approximation in the computation of C-H···anion interactions in general.

2) Binding energy

In the previous section, the CN^--methane complex was found to be bound. We now calculate the binding energies of the two minimum colinear arrangements accurately by employing extensive basis sets, which include the near Hartree-Fock limit basis set [10s7p3d/7s2p] of Lee and Shaeffer [10]. In our SCF and MP2 calculations with those basis sets, the fragment geometries were frozen but the interfragment distances r_{NH} and r'_{CH} were optimized. At the computed minima, the binding energies with and without counterpoise correction of the BSSE ($D_{e,CP}$ and D_e, respectively) are calculated. The values of the harmonic stretching vibrational frequences (ω) of the $CN^-\cdots$methane complex, computed assuming that the fragments behave as two pseudoparticles, are also calculated. The D_e, $D_{e,CP}$, and ω

values for each basis set studied are included in Table 3 for the linear $CN^-\cdots H\text{-}CH_3$ arrangement (**1**), and Table 4 for the linear $NC^-\cdots H\text{-}CH_3$ arrangement (**2**).

Table 3 shows that the [10s7p3d/7s2p] basis set presents a negligible BSSE at the SCF level. At the MP2 level, the BSSE error is slightly larger, as expected [4]. Table 3 also shows that the BSSE's in both the SCF and MP2 methods generally become smaller as the basis set quality is increased. The difference between D_e and $D_{e,CP}$ (i.e., the BSSE) can be a measure of the error caused by the incompleteness of the basis set employed, one of the two components of the BSSE [7]. At the MP2 level, the BSSE for the near Hartree-Fock basis set is about 0.1 kcal/mol. Therefore, the best estimate of the MP2 binding energy of the $CN^-\cdots H\text{-}CH_3$ arrangement is 2.6 ± 0.1 kcal/mol. With the same basis set, the best estimate of the SCF binding energy of the same system is 1.75 ± 0.01 kcal/mol. The MP2 binding energy is about 50% larger than the SCF binding energy.

It is interesting to note from Table 3 that the average values of D_e and $D_{e,CP}$ obtained with the 6-31++G(2d,2p) and 6-311++G(2d,2p) basis sets are similar to the corresponding values obtained with the near Hartree-Fock basis set at the SCF and MP2 levels. On the basis of this observation and Table 4, the best estimates of the SCF and MP2 binding energies for the $NC^-\cdots H\text{-}CH_3$ arrangement are 1.34 and 2.3 kcal/mol, respectively.

The zero point corrections for these binding energies can be obtained from the stretching frequencies ω assuming that the zero point energies of the fragments remain constant in the complex. Then, at the MP2 level, the zero point corrected binding energies of the $CN^-\cdots H\text{-}CH_3$ and $NC^-\cdots H\text{-}CH_3$ arrangements are estimated to be 2.5 and 2.1 kcal/mol, respectively.

Finally, notice from Table 3 that, with the smallest basis set employed, i.e., the 6-31++G(d,p), the $D_{e,CP}$ value deviates more from the best estimate of the binding energy than does the D_e value. As this example shows, the $D_{e,CP}$ values not always are better estimates for the true binding energies than are the corresponding D_e values.

3) Vibrational analysis

In order to justify the validity of the simplified zero point corrections for the two minimum energy colinear arrangements of the CN^-···methane complex, we carried out full vibrational analyses of the two arrangements at their fully optimized geometries using the SCF and MP2 methods with the 6-31++G(d,p) basis set. The harmonic vibrational frequencies, and infrared intensities of all the vibrational modes computed for the monomers and the CN^-···H-CH_3 arrangement are included in Table 5, and those for the NC^-···H-CH_3 arrangement in Table 6.

Tables 5 and 6 show the existence of two types of vibrations for each arrangement. The lowest five vibrational modes are intermolecular (interfragment) in nature and fall within the far-infrared region of the spectrum (10-350 cm^{-1}), as expected from the magnitude of the binding energy of the arrangement [11]. The other vibrations, which occur at much higher frequencies, are intramolecular (intrafragment) in nature because they have a one-to-one correspondence with the modes present in the isolated fragments (except for some split and small shift).

In Table 5, the A_1 mode with SCF frequency of 82 cm^{-1} corresponds to the ν_σ stretching [12] between the CN^- and CH_4 fragments, and the two E

modes of SCF frequency 25 cm^{-1} correspond to the two ν_β [12] degenerate angular deformations of the CN^- fragment relative to the methane. The corresponding MP2 values for those modes are at 100 and 19 cm^{-1}, respectively. The SCF A_1 stretching frequency of Table 5 (82 cm^{-1}) is almost identical with the corresponding value in Table 3 (89 cm^{-1}) computed with the pseudoparticle approach. The same is also true for the MP2 frequencies (100 cm^{-1} in the full MP2 vibrational analysis and 121 cm^{-1} in the pseudoparticle analysis of Table 3). Similar results are found for the $NC^-\cdots H\text{-}CH_3$ arrangement: 65 cm^{-1} in the full vibrational analysis (Table 6) and 60 cm^{-1} in the pseudoparticle analysis (Table 4). Therefore, the pseudoparticle vibrational analysis provides good estimates of the two ν_σ stretching frequencies.

Tables 5 and 6 also show that the ν_s C-H stretching mode [12] of the two arrangements is red shifted respect to the corresponding value of CH_4 by about 30 cm^{-1} at the SCF and MP2 levels. Although the shift is small, it is well within the 10-150 cm^{-1} range observed for the complexes of alkynes and alkenes with molecules containing second and third row heteroatoms [13]. This red shift is characteristic of a very weak hydrogen bond [11].

The SCF and MP2 frequencies of all the systems studied here are very similar, except for the C-N stretching which presents a change of about 400 cm^{-1}. The intensities of the vibrational modes are also similar at SCF and MP2 values, except for some of the A_1 modes and the Σ_g vibration of the CN^- fragment. Though not shown, the 6-31++G(2d,2p) basis set leads to results similar to those obtained with the 6-31++G(d,p) basis set.

Concluding remarks

Using the SCF and MP2 methods we have shown that the CN^-···methane complex is bound, with two minima corresponding to the linear CN^-···H-CH_3 and NC^-···H-CH_3 arrangements. At the MP2 level, with the zero point energy correction, the binding energy of these two structures are estimated to be 2.5 ± 0.1 and 2.1 ± 0.1 kcal/mol, respectively. Full vibrational analyses of both arrangements show a red shift of about 30 cm^{-1} for the ν_s C - H strectching.

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Table 1

Optimized geometry (in Å and degrees) and total energy (E, in a.u.) for the $CN^-\cdots H\text{-}CH_3$ (1) arrangement and its fragments computed at the SCF and MP2 levels using the 6-31++G(d,p) and 6-31++G(2d,2p) basis sets. The dissociation energy of the complex (D_e, in kcal/mol) is also included.

	SCF		MP2	
	6-31++G(d,p)	6-31++G(2d,2p)	6-31++G(d,p)	6-31++G(2d,2p)
CN^-				
r_{CN}	1.162	1.158	1.201	1.196
E	-92.314872	-92.319323	-92.603403[a]	-92.626304[a]
CH_4				
r_{CH}	1.084	1.083	1.085	1.086
∢HCH	109.47	109.47	109.47	109.47
E	-40.202169	-40.204253	-40.366110[a]	-40.380388[a]
$CN^-\cdots CH_4$				
r_{NH}	2.630	2.634	2.478	2.387
θ	0.	0.	0.	0.
r_{CN}	1.162	1.158	1.200	1.195
r_{CH}	1.086	1.085	1.088	1.088
∢HCH	109.83	109.86	108.85	109.87
E	-132.519850	-132.526376	-132.973464[a]	-133.011200[a]
D_e	1.76	1.76	2.48	2.82

[a] From a frozen core MP2 calculation.

Table 2

Optimized geometry (in Å and degrees) and total energy (E, in a.u.) for the $NC^-\cdots H\text{-}CH_3$ arrangement computed at the SCF level using the 6-31++G(d,p), 6-31++G(2d,2p), and 6-311++G(2d,2p) basis sets. The dissociation energy of the complex (D_e, in kcal/mol) is also included.

	6-31++G(d,p)	6-31++G(2d,2p)	6-311++G(2d,2p)
r_{NH}	2.958	2.985	2.958
θ	0.	0.	0.
r_{CN}	1.161	1.158	1.162
r_{CH}	1.085	1.085	1.091
$\sphericalangle$HCH	109.76	109.77	108.50
E	-132.519290	-132.525816	-132.552832
D_e	1.41	1.41	1.61

Table 3

Optimized interfragment distance (r_{NH}, in Å), total energy (E, in a.u.), dissociation energy (D_e, in kcal/mol), BSSE corrected dissociation energy ($D_{e,CP}$, in kcal/mol), and stretching frequency (ω, in cm^{-1}) computed with various basis sets at the SCF and MP2 levels for the colinear arrangement $CN^-\cdots H\text{-}CH_3$ (**1**), and with frozen fragment geometries.

Basis set		r_{NH}	E	D_e	$D_{e,CP}$	ω
6-31++G(d,p)	SCF	2.652	-132.519772	1.77	1.69	89
	MP2	2.489	-132.970447[a]	2.54	2.07	121
6-31++G(2d,2p)	SCF	2.655	-132.526245	1.80	1.66	90
	MP2	2.439	-133.008862[a]	2.91	2.31	113
6-311++G(2d,2p)	SCF	2.672	-132.553061	1.75	1.71	91
	MP2	2.451	-133.052454[a]	2.83	2.45	114
[10s7p3d/7s2p]	SCF	2.670	-132.565330	1.75	1.74	91
	MP2	2.457	-133.085646[a]	2.76	2.63	116

[a] From a frozen core MP2 calculation.

Table 4

Optimized interfragment distance (r'_{CH}, in Å), total energy (E, in a.u.), dissociation energy (D_e, in kcal/mol), BSSE corrected dissociation energy ($D_{e,CP}$, in kcal/mol), and stretching frequence (ω, in cm^{-1}) computed with various basis sets at the SCF and MP2 levels for the colinear arrangement $NC^{-}\cdots H\text{-}CH_3$ (**2**), and with frozen fragment geometries.

Basis set		r'_{CH}	E	D_e	$D_{e,CP}$	ω
6-31++G(d,p)	SCF	2.975	-132.519192	1.44	1.24	60
	MP2	2.770	-132.969906[a]	2.20	1.74	77
6-31++G(2d,2p)	SCF	3.004	-132.525663	1.43	1.29	63
	MP2	2.737	-133.007990[a]	2.35	1.96	74
6-311++G(2d,2p)	SCF	3.001	-132.552437	1.36	1.33	63
	MP2	2.678	-133.051812	2.43	2.17	102

[a] From a frozen core MP2 calculation.

Table 5

Symmetry, frequency (ω, in cm^{-1}), and infrared intensity (I, in kM/mol) of the normal modes calculated at the SCF and MP2 levels with the 6-31++G(d,p) basis set for the minimum $CN^-\cdots H\text{-}CH_3$ arrangement (**1**) and its fragments. The experimental value of the frequency, when available, is also given for comparison.

	SCF		MP2		Expt.
Symmetry	ω	I	ω	I	ω
CN^-					
Σ_g	2330	48	1991	3	2080-2239[a]
CH_4					
T_2	1463	12	1397	15	1357[a]
E	1673	0	1594	0	1573[a]
A_1	3169	0	3122	0	3143[a]
T_2	3276	43	3269	23	3154[a]
$CN^-\cdots H\text{-}CH_3$					
E	25	0	19	1	
A_1	82	24	100	25	
E	163	0	152	0	
A_1	1431	7	1360	9	
E	1485	10	1419	11	
E	1680	1	1599	2	
A_1	2331	59	1993	5	
A_1	3143	51	3089	69	
E	3243	83	3235	51	
A_1	3273	5	3246	24	

[a] Reference [14]

Table 6

Symmetry, frequency (ω, in cm^{-1}), and infrared intensity (I, in kM/mol) of the normal modes calculated at the SCF level with the 6-31++G(d,p) basis set for the minimum $NC^{-}\cdots H\text{-}CH_3$ arrangement (**2**).

Symmetry	ω	I
$NC^{-}\cdots CH_4$		
E	28	2
A_1	65	21
E	154	1
A_1	1434	8
E	1483	10
E	1679	1
A_1	2335	47
A_1	3148	37
E	3248	77
A_1	3275	0

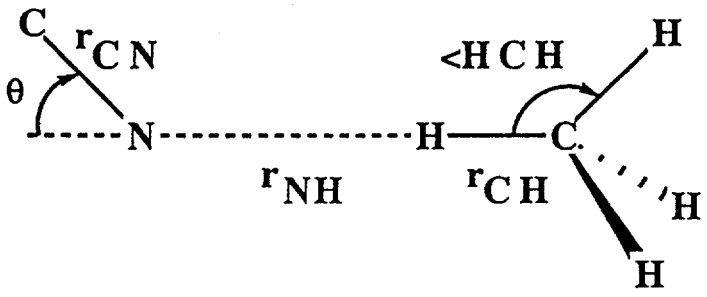
Figure captions

Figure 1.

Potential energy surface computed at the SCF level with the 6-31++G(d,p) basis set for (a) the $CN^-\cdots H\text{-}CH_3$ arrangement (**1**), (b) the $NC^-\cdots H\text{-}CH_3$ arrangement (**2**), and (c) the $CN^-\cdots$methane arrangement **3**. The values of r_1 and r_2 (both in Å) in (a) are defined as $r_1 = r_{NH}\cdot\cos\theta$ and $r_2 = r_{NH}\cdot\sin\theta$, and those in (b) are defines as $r_1 = r'_{CH}\cdot\cos\theta$, and $r_2 = r'_{CH}\cdot\sin\theta$. The values of the contours plotted (in kcal/mol) are indicated at the right-hand-side margin. The values are those encountered moving away from the minimum. The energies given respect to the energy of the optimum $CN^-\cdots H\text{-}CH_3$ arrangement, which is shown in (a) by a the symbol •.

Figure 2.

(a) Energy of the colinear $CN^-\cdots H\text{-}CH_3$ arrangement (**1**) as a function of the r_{NH}, computed at the SCF and MP2 levels.
(b) Energy of the $CN^-\cdots H\text{-}CH_3$ arrangement (**1**) as a function of the angle θ, computed at the SCF and MP2 levels, with the r_{NH} distance fixed at the optimum MP2 value of 2.489 Å.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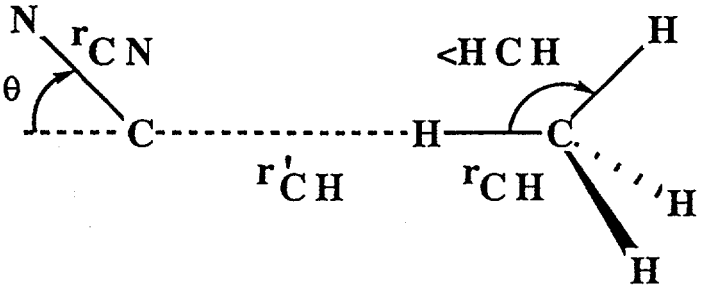
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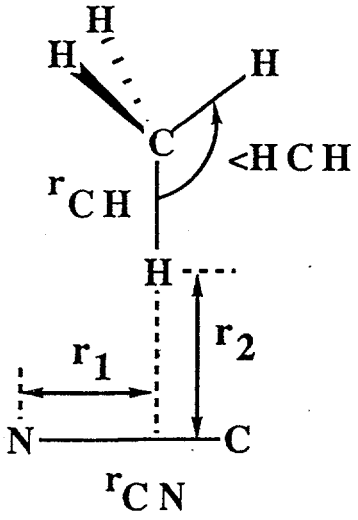
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3

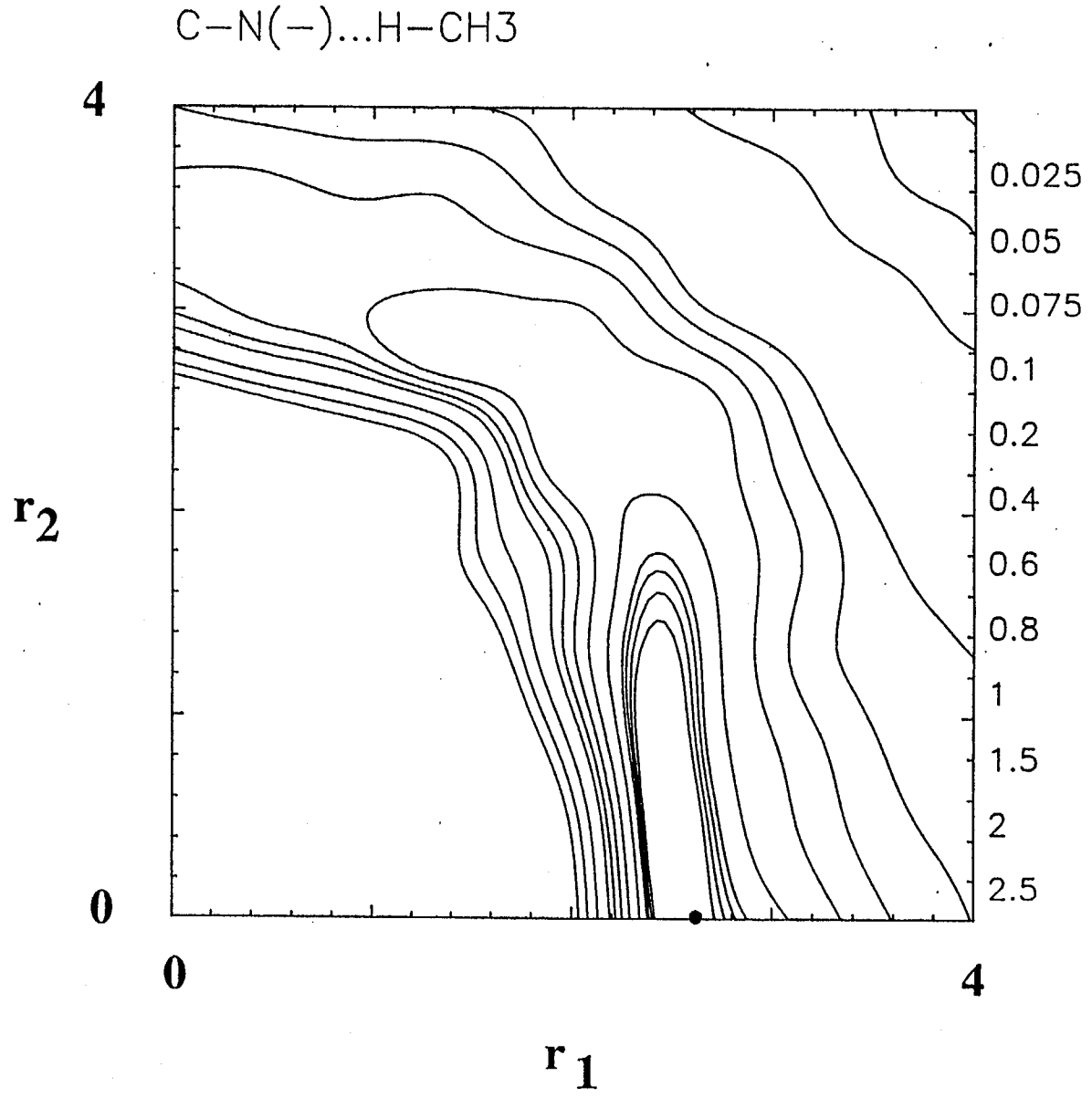

Fig 1.a

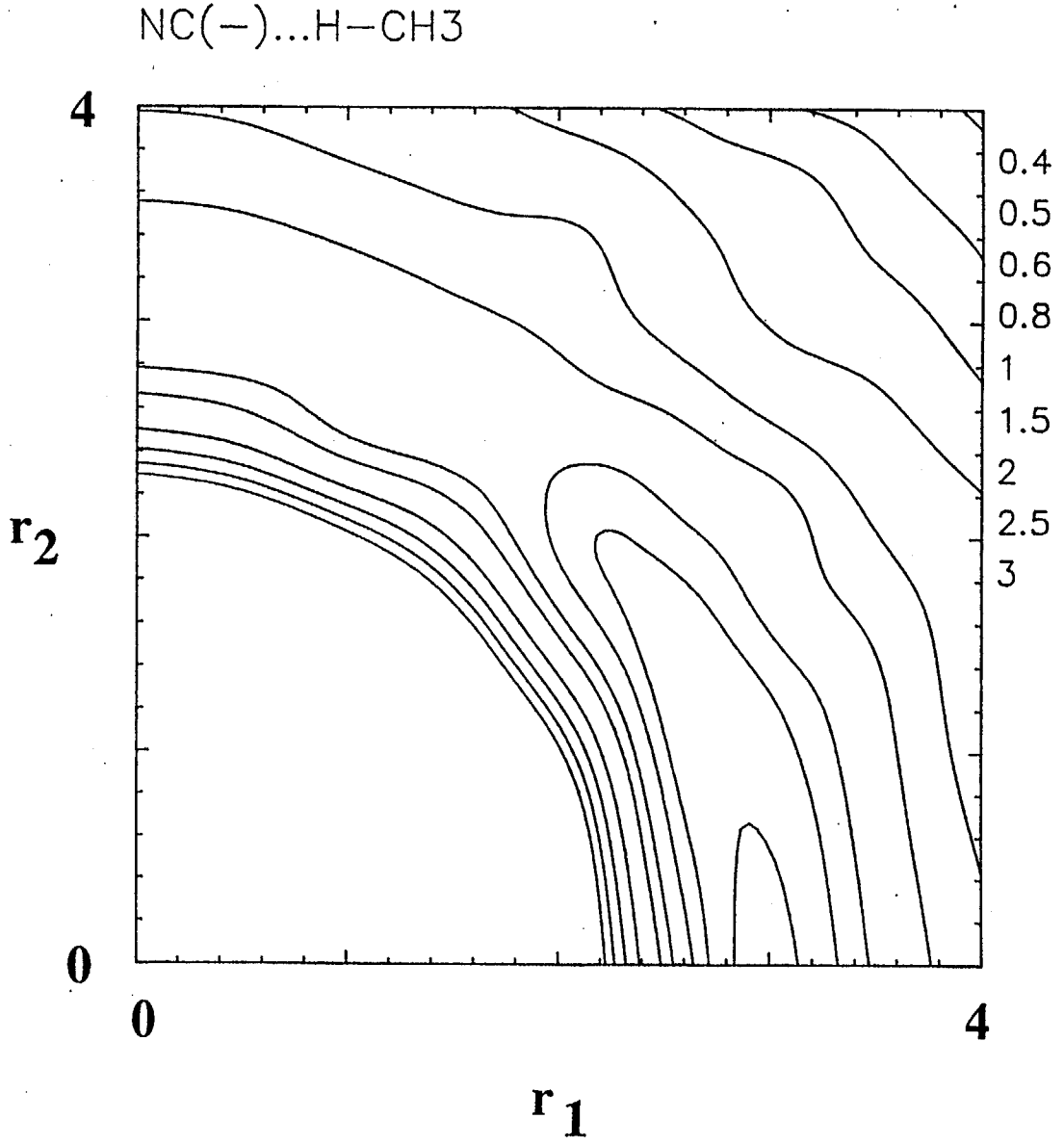

Fig 1.6

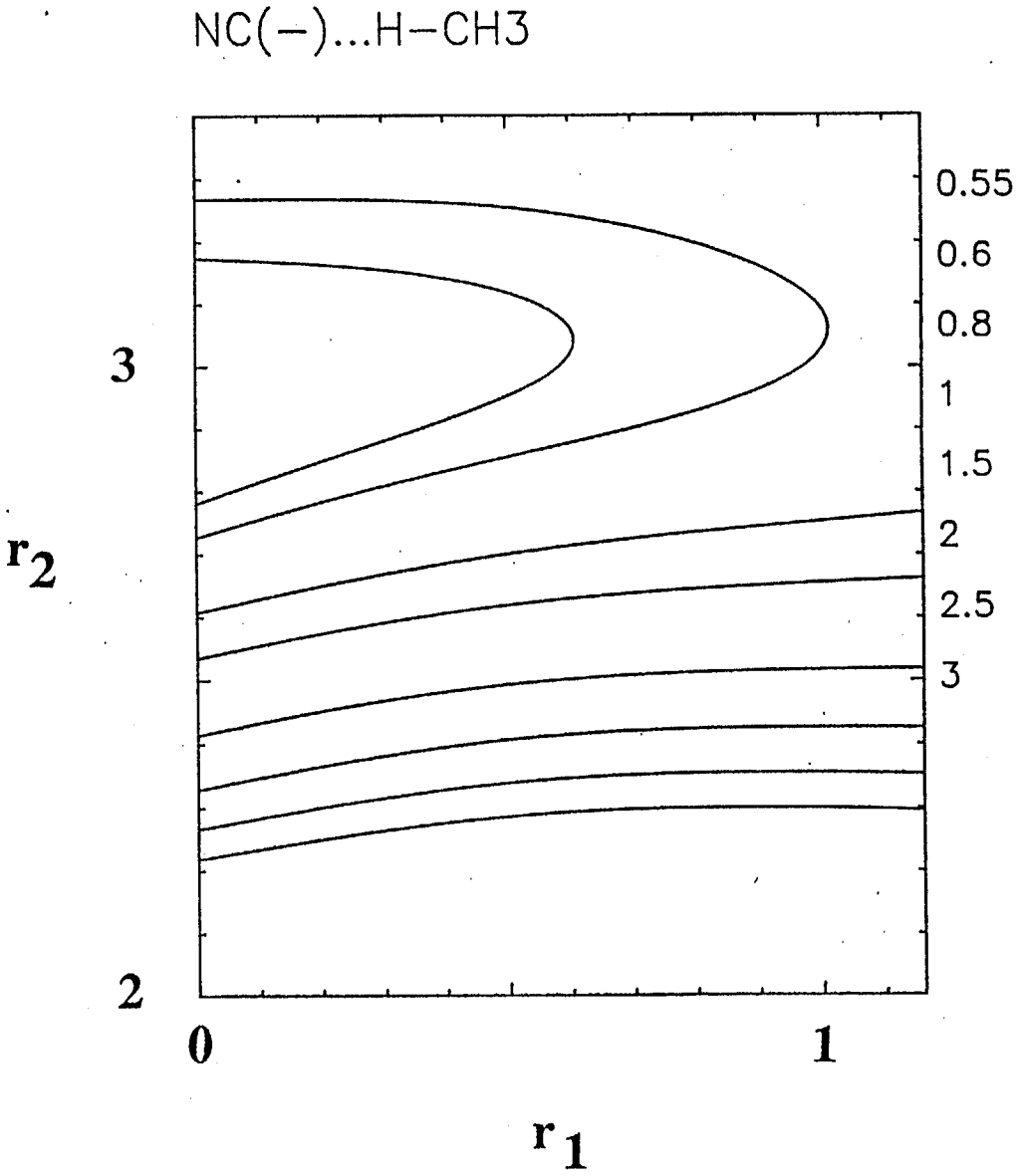

Fig 1.c

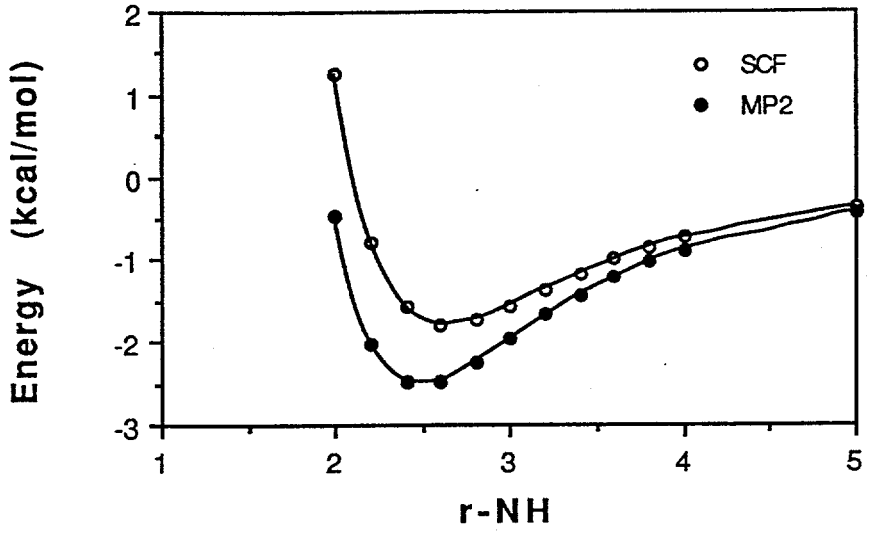

Fig 2.a

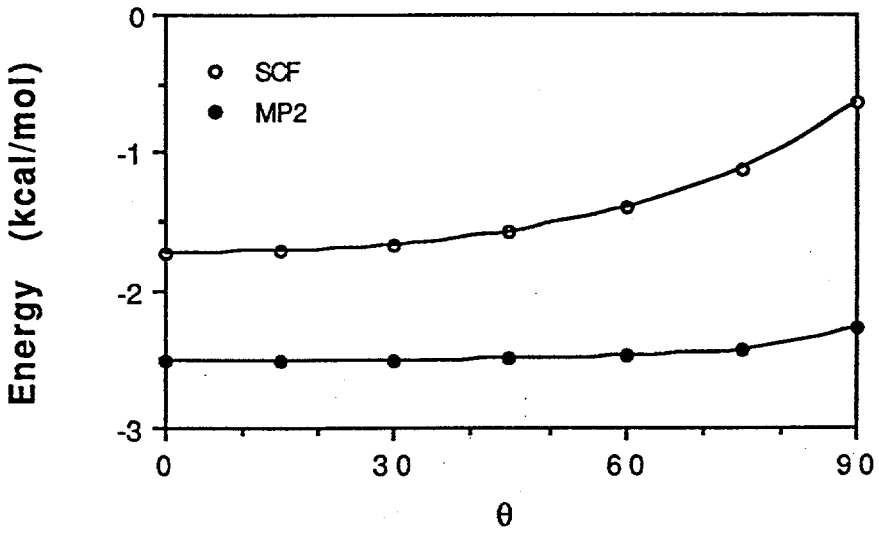

Fig 2.5.