Theor Chem Acc (1998) 100:300–306
DOI 10.1007/s002149800m64

Theoretical
Chemistry Accounts
© Springer-Verlag 1998

Regular article

Complexes of ammonia with propane and cyclopropane: electrostatic guidelines for ab initio treatment

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Received: 8 July 1998 / Accepted: 4 August 1998 / Published online: 2 November 1998

Abstract. A model based on the molecular electrostatic potential (MESP) is employed for the investigation of structures and energies of complexes of ammonia with propane and cyclopropane. The electrostatic model geometries are employed as starting points for an ab initio investigation at the self-consistent field and second-order Møller-Plesset (MP2) levels. The most stable structures of $C_3H_6..NH_3$ and $C_3H_8..NH_3$ complexes have the interaction energies of 10.07 kJ/mol and 8.15 kJ/mol, respectively, at the MP2/6-31G(*d,p*) level. The energy rank order of the structures is not altered with the use of the 6-31++G(*d,p*) basis set, and the basis set superposition error has little effect. The interaction energy decomposition analysis shows that the electrostatic component is dominant over the other ones. MESP topography thus seems to offer valuable hints for predicting the structures of weakly bonded complexes.

Key words: Topography – Molecular electrostatic potential – Critical point – ab initio calculations

1 Introduction

Van der Waals (vdW) and H-bonding interactions are found to be of great importance in many aspects of chemical, biological and atmospheric science. As a consequence, a large number of investigations are being carried out on these complexes especially exploring their structure, energetics and spectroscopic properties [1]. These complexes have been experimentally investigated mainly using vibrational and microwave spectroscopy in the gas phase. Ab initio methods have been extensively employed both for the prediction of geometry and interaction energy of many vdW complexes and for understanding the nature of the weak interactions involved. Electrostatic and charge transfer interactions are mainly responsible for the formation of such weak intermolecular complexes. Results of the interaction energy decomposition [2] show that the electrostatic part is many a time dominant one over the others such as dispersion and charge transfer. Legon and Millen [1] have commented that the angular geometry of the vdW complex is determined largely by the angular variation of the electrostatic potential. In view of the electrostatic nature of the interaction, various models have been developed for studying such vdW complexes [3–5]. They yield reasonable estimates of the energies of the complexes as well as fairly good prediction of their geometries. For the weak complexes, these models may yield good guess geometry for ab initio calculations. Recently, Gadre et al. [6] have developed a model, termed the electrostatic potential for intermolecular complexation (EPIC) model based on the molecular electrostatic potential and its topography (discussed in the next section) for the study of weak complexes. This model is generally seen to yield good prediction of geometry and energetics of the complex. In the present study, the EPIC model is utilized as a predictive tool for the study of complexes of ammonia with cyclopropane and propane.

It has been conjectured that the anesthetic nature of cyclopropane (C_3H_6) results from its molecular association. To verify this, various complexes of cyclopropane have been studied. For example, complexes with HF, HCl, HCN, H_2O and SO_2 have been explored in recent years [7]. In the first four cases, H in the acid molecule is bonded to the centre of C-C bond, with the HX in the CCC plane. These results qualitatively support the Coulson and Moffitt [8] bent banana bond model of cyclopropane. However, in a recent study using microwave spectroscopy, Forest and Kuczkowski [9] have shown that the $C_3H_6..NH_3$ complex does not conform to this pattern, where the C_3H_6 acts as a proton donor. Taking their results into consideration, a question arises [9] regarding the binding of ammonia with propane which lacks these bent-bond features. In the present work, we investigate these complexes using the EPIC model followed by an ab initio investigation for determining various structures and their interaction energies.

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The procedure employed for the study is discussed below.

2 Method

The geometries of monomers were optimized at the Hartree-Fock (HF), self-consistend field (SCF) and second-order Møller-Plesset (MP2) levels of ab initio theory using the 6-31G(*d*,*p*) and 6-31++G(*d*,*p*) basis sets. It has been shown that the former basis set is normally adequate for treatment of such medium-sized molecules [10]. The corresponding density matrix elements were utilized for the determination of potential-derived atomic charges (PD-ACs) and the critical points (CPs) in the molecular electrostatic potential (MESP) of monomers. A model based on the PD-AC, CP information and MESP of monomers was used for determining the structures and interaction energies of the complexes formed by the monomers. These structures were used as an initial guess for the full geometry optimization. A brief description of the MESP and the EPIC model is given below.

The MESP V(**r**) at a point r due to nuclear charges $\{Z_A\}$ at $\{\mathbf{R}_A\}$ and the electronic density $\rho(\mathbf{r})$ of the molecule is given by

$$V(\mathbf{r}) = \sum_A \frac{Z_A}{|\mathbf{R}_A - \mathbf{r}|} - \int \frac{\rho(\mathbf{r}')}{|\mathbf{r}' - \mathbf{r}|} d^3r' \ . \tag{1}$$

The first term of the equation represents the bare nuclear potential while the second term denotes the electronic part of the potential. The MESP has been widely used as a tool for monitoring chemical reactivity [11] and molecular interaction [12]. In recent years, Gadre et al. [13] have initiated the use of topography for identifying the salient structural features of molecules. The topography of MESP is described in terms of minima and saddle points. These points are known as CPs [14], the points at which $\nabla V(r) = 0$, which physically means that the internal electric field vanishes at the CP.

As mentioned above, the EPIC [6] model has been used for the determination of structure and energy of the complex. The interaction energy of the complex formed by monomers A and B is given by

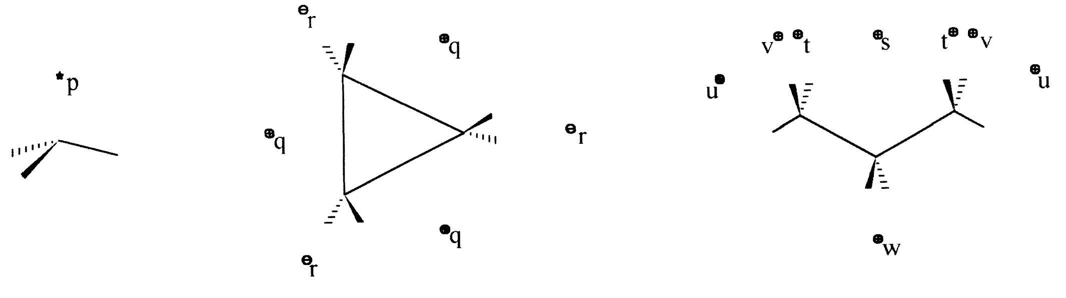
$$(1/2)\left\{\sum V_{A,i}\, q_{B,i} + \sum V_{B,i}\, q_{A,i}\right\} \ , \tag{2}$$

where $V_{A,i}$ is the MESP value due to A at the ith atom of molecule B and $q_{B,i}$ is the PD-AC on the ith atom of B. Similarly, $V_{B,i}$ is the MESP value due to B at the ith atom A and $q_{A,i}$ is the PD-AC on the ith atom of A. The minimum energy structure is searched for by complete translation and rotation of the molecule B with respect to A and by minimizing the energy in Eq.(2). Use of vdW radii [15] for atoms prevents the collapse of the two species. An appropriately chosen radius was employed for the hydrogen atom.

All the ab initio calculations and Morokuma analyses were performed using the INDMOL [16] and GAMESS [17] software packages on Reduced Instruction Set Computer (RISC) work stations. The MESP was evaluated using the indigenously developed INDPROP [13] package. The GRID program [18] was used to analyse the PD-ACs.

3 Results and discussion

Figure 1 depicts the negative-valued MESP CPs of NH_3 (Fig. 1a), C_3H_6 (Fig. 1b) and C_3H_8 (Fig. 1c) molecules. The CPs show the electron-rich regions of the hydrocarbons and lone pair of NH_3. The CP parameters viz. nature, MESP at the CP and the distance from centre of mass are listed in Table 1. In C_3H_6, minima and saddle CPs are encountered on each of the C_2 axes with the minima and saddle point near to the CC edge and ring carbon, respectively. A numerically large value (–71 kJ/mol) at the minimum indicates a probable proton acceptor site. On the other hand, a numerically smaller MESP value (–2.0 kJ/mol) at the saddle point shows unequal charge distribution in the CCC plane. The C_3H_8 molecule also possesses negative-valued MESP minima and saddle points. However, here the MESP distribution is more uniform, wherein the MESP values at the CPs vary by ±1 kJ/mol from their mean value. This is an indication that C_3H_8 may be less reactive than C_3H_6 and hence leads to weak intermolecular interaction with ammonia. In NH_3, only one type of CP is engendered on the C_3 axis above the N atom with a very large



(a) (b) (c)

Fig. 1a–c. Location of negative-valued molecular electrostatic potential critical points (CPs) of monomers (**a**) NH_3 (**b**) C_3H_6 and (**c**) C_3H_8. Here **p**, **q**, **r**, **s**, **t**, **u**, **v** and **w** indicate the CPs detailed parameters which are reported in Table 1

MESP value (–358 kJ/mol). The location and MESP value at the CP implies that NH_3 is a proton acceptor. This result is supported by experimental studies [19].

In the present work, the initial geometries of the propane..NH_3 complexes for the EPIC model were prepared by placing the H atom of propane in the vicinity of the CP of NH_3, or the H atom of NH_3 near to the CP of propane. Some starting geometries were generated by placing the N atom of the ammonia molecule constrained on the C_3 axis, facing the relatively electron deficient region of the cyclopropane ring. The model computation as described in Sect. 2 was carried out for different possible geometries. Five different structures each of C_3H_6..NH_3 and C_3H_8..NH_3 were located by minimizing the EPIC interaction energy given by Eq.(2). The interaction energy (E_{INT}) and the distance between N and the centre of mass (CM) of C_3H_6 or C_3H_8 ($R_{CM..N}$) are presented in Table 2. The gradients of total energy with respect to the model geometry are also given in Table 2. The gradients are in the range of 0.002–0.009 a.u. indicating that the model geometry can be used to make an initial guess for the full ab initio optimization. However, the atomic hard spheres that are used to limit the EPIC interaction energy, constrain the orientation of NH_3 (position of H atoms). To obtain a proper orientation of NH_3, the model geometry was further refined by an SCF docking process. In this process, the internal geometries of two interacting molecules are held intact and the position and orientation of one of them is changed relative to other. This docking method has been found quite useful for facilitating the approach to minimum energy structures.

Table 1. Molecular electrostatic potential (MESP) critical point (CP) parameters of C_3H_6, C_3H_8 and NH_3 with the 6-31G(*d,p*) basis set. $R_{CM..CP}$ is the distance from the centre of mass of the molecule to the CP. V_{CP} is the MESP at the CP. (3, + 3) and (3, + 1) indicate the minima and saddle point, respectively. p,q,... denote the positions of CPs in Figs. 1 and 2. The numbers in the brackets show the number of symmetric CPs

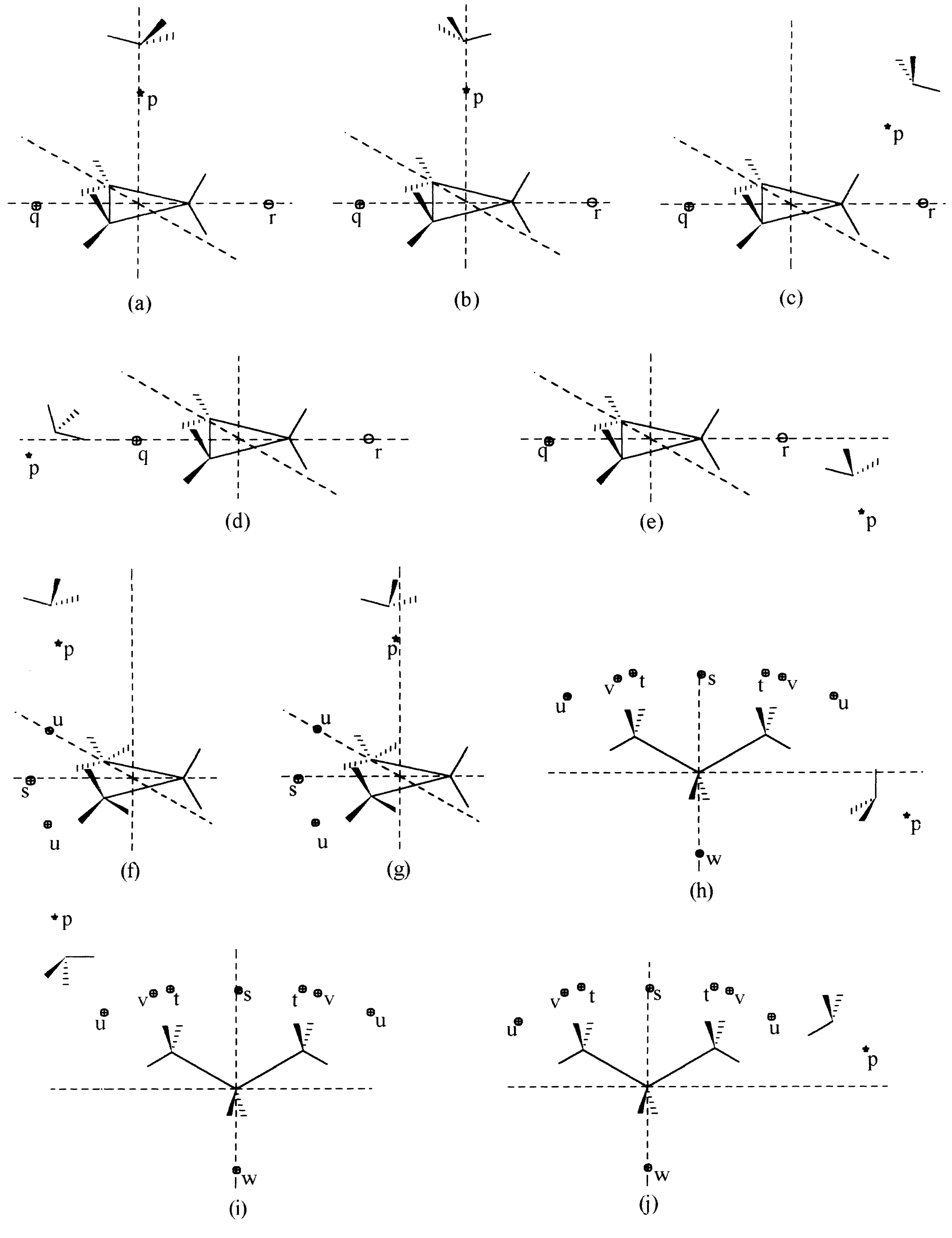
Molecule	CP type	$R_{CM..CP}$ (Å)		V_{CP} (kJ/mol)	
		SCF	MP2	SCF	MP2
NH_3	(3, + 1) (p) [1]	1.20	1.31	−358.25	−317.31
C_3H_6	(3, + 3) (q) [3]	1.92	1.92	−71.47	−71.50
	(3, + 1) (r) [3]	3.19	3.20	−2.23	−2.21
C_3H_8	(3, + 1) (s) [1]	2.21	2.11	−9.72	−11.06
	(3, + 3) (t) [2]	2.66	2.31	−11.62	−11.28
	(3, + 3) (u) [2]	3.27	3.28	−12.06	−11.56
	(3, + 1) (v) [2]	2.79	2.86	−11.61	−10.58
	(3, + 3) (w) [1]	2.59	2.62	−10.34	−9.10

The docked model geometries were further optimized by ab initio HF-SCF and MP2 level calculations. The fully optimized structures and their energies are presented in Table 2 (symmetry-related geometries are excluded). The nature of structures (whether a minimum, transition state or saddle point) was identified by carrying out frequency calculations. The results show that the electrostatic model is able to yield sufficiently correct information about the interaction energy and geometry of dimers, with negligible computational effort.

The stacked structure in which the lone-pair electrons of ammonia interact with the hydrogen atoms above the ring is more stable than other H-bonded structures. In this "inverted umbrella" structure, the hydrogen atoms of ammonia are either eclipsed (Fig. 2b) or staggered (Fig. 2a) with respect to the H of C_3H_6. The staggered form is found to be a global minimum (interaction energy, $E_{INT} = -10$ kJ/mol) with a very small energy difference from the eclipsed one. In these two structures, ammonia acts as an electron donor. The E_{INT} is found to be consistent with the reported energies of hydrocarbon..ammonia: –17 kJ/mol for C_4H_2..NH_3 [20] and −10 kJ/mol for C_6H_6..NH_3 [21]. In another structure, ammonia is the proton acceptor, with an N atom sitting above the H of C_3H_6 (Fig. 2c) and the energy is comparable to the staggered form. In the last two structures (Fig. 2d, e) listed in Table 2 ammonia acts as a proton donor with its H atom lying near to the MESP CP of C_3H_6. These structures are found to be less stable than those where ammonia acts as a proton acceptor.

Table 2. Structural and energy parameters of complexes of ammonia with cyclopropane (**a**–**e**) and propane (**f**–**j**). $R_{CM..N}$ is the distance between the N atom and the centre of mass of cyclopropane or propane. G is the maximum self-consistent field (SCF) gradient norm in a.u. at the model-optimized geometry. N_{IF} is the number of imaginary frequencies. E_{INT} is the interaction energy calculated at the 6-31G(*d,p*) (1) and 6-31++G(*d,p*) (2) basis set levels. Distances and energies are in Å and kJ/mol, respectively

Complex	$R_{CM..N}$				E_{INT}				G	N_{IF}	
	Model (1)	SCF (1)	MP2 (1)	SCF (2)	Model (1)	SCF (1)	MP2 (1)	SCF (2)		SCF (1)	MP2 (1)
a	3.12	3.80	3.46	4.08	−8.35	−4.80	−10.07	−2.43	0.003	0	0
b	3.06	3.80	3.47	4.11	−8.17	−4.69	−9.96	−2.36	0.002	0	1
c	3.62	4.47	4.17	4.49	−6.46	−4.25	−8.10	−2.23	0.006	0	1
d	3.64	4.32	4.00	4.37	−6.22	−2.52	−7.34	−2.02	0.006	0	2
e	3.52	4.37	3.98	4.38	−4.56	−2.44	−7.43	−2.08	0.004	1	3
f	3.82	4.15	3.81	4.37	−2.63	−3.82	−8.15	−1.17	0.007	0	0
g	3.67	3.99	3.72	4.53	−2.51	−3.60	−8.10	−0.87	0.007	1	1
h	4.85	5.34	4.97	5.52	−0.61	−1.77	−5.58	−0.72	0.007	0	1
i	4.23	5.29	4.66	5.85	−1.25	−0.85	−6.09	+ 0.16	0.003	1	0
j	4.57	5.96	5.91	5.92	−1.46	−0.30	−3.76	+ 0.07	0.009	5	–



(a) (b) (c) (d) (e) (f) (g) (h) (i) (j)

Fig. 2a–j. The van der Waals complexes of NH_3 with C_3H_6 and C_3H_8. (**a–f**: $C_3H_6..NH_3$, **f–j**: $C_3H_8..NH_3$). See text for details

Forest and Kuczkowski [9] investigated the $C_3H_6..NH_3$ complex experimentally using Fourier Transform Microwave (FTMW) spectroscopy and showed that the ammonia molecule acts as a proton acceptor. The $R_{CM..N}$ is found to be in good agreement with their value (3.66 Å) for the staggered confomer. They also determined the interaction energy using the Buckingham-Fowler (B-F) model, which is conceptually and computationally simple. In the B-F model [3], the energy is calculated from the multipoles placed at the atom centres. The multipoles are determined from the distributed multipole moments analysis of the respective charge densities [22]. According to the B-F model the energies for the staggered and eclipsed forms are –1.05 and –0.49 kJ/mol, respectively, showing the correct rank order, viz. a staggered form is more stable than an eclipsed form. However, the EPIC model energy at these points better mimics the corresponding SCF one (cf. Table 2).

The results of $C_3H_6..NH_3$ are found to be different from the conventional complexes of C_3H_6, in which it acts as a hydrogen acceptor with a hydrogen lying near to the CCC plane. In view of this, it is interesting to compare the above results with those for ammonia complexes with propane. The MESP CPs of C_3H_8 show that the electron distribution is not localized (cf. Table 1). As a consequence of this, weak interaction is expected. However, the results of complexation with ammonia show that the interaction energy is comparable to that of a cyclopropane-ammonia complex. It indicates that polarization and charge transfer phenomena may be significant for this complex. The results for the $C_3H_8..NH_3$ complex are listed in Table 2. The ammonia umbrella pointed up with N above the midpoint of the terminal C atom is found to be more stable (cf. Fig. 2f). The interaction energy is found to be numerically less than the corresponding $C_3H_6..NH_3$ one. Near to this global minimum, a transition state (Fig. 2g) has been observed with comparable energy. In other structures, it acts as a proton donor with the hydrogen near to the MESP CP of C_3H_8 and the energy is much less. These H-bonded structures lie in the vicinity of CCC plane of C_3H_8. The structure in which hydrogen atoms of NH_3 are eclipsed to the CH_3 group of C_3H_8 (Fig. 2j) is found to be less stable than the staggered one (Fig. 2i). Table 1 gives a comparison of CPs of C_3H_6 and C_3H_8. Various CPs with nearly equal MESP values of C_3H_8 are found in the plane of molecule. Their location suggests that there are various possible complexes with ammonia. The MESP value at its CPs is about seven times less than the MESP minimum of C_3H_6, indicating relatively less reactivity therefore causing difficulty in the search for the most stable structure of $C_3H_8..NH_3$.

In order to examine the effect of the basis set, the above calculations were repeated with a 6-31++G(*d,p*) basis set. The SCF-optimized results are presented in Table 2. At this basis level, the interaction energy is found to be numerically less than that for the corresponding 6-31G(*d,p*) basis set. However, the rank order and number of imaginary frequencies of the structures are not changed. The "i" and "j" complexes turn out to be unstable at this level. To check the effect of using a larger basis set, calculations at the MP2/6-31++G(*d,p*) level were also carried out for some complexes. For the structures "a" and "b", the interaction energies at the MP2/6-31++G(*d,p*) basis set level were found to be −8.07 and −7.95 kJ/mol, respectively. At this level, the $R_{CM\cdot\cdot N}$ distances were 3.56 and 3.61 Å for the "a" and "b" structures, respectively. The energies and distances for the "f" and "g" structures at the MP2/6-31++G(*d,p*) level were (−5.49 kJ/mol, 3.87 Å) and (−4.0 kJ/mol, 3.9 Å), respectively. It is noteworthy that there was no change in the rank order of the energies which were typically shifted upwards by 2 kJ/mol.

The results in Table 2 show that the two species approach closer at the MP2 level. This is in agreement with the general trend for other vdWs complexes [23] which has been attributed to the fact that MP2 calculations take into account attractive dispersion forces, leading to the decrease of H-bond length [24]. Further, as expected, MP2 interaction energies are numerically larger (typically double or more) than the corresponding SCF ones. However, the lowest and highest energy structures at the SCF and MP2 levels generally match. It has been noted earlier [25] that the MP2 calculations are capable of yielding good results for intermolecular distance and energy, and that for the weak complexes the higher-order MP terms do not show significant change. How does the MESP topography change on the incorporation of correlation? The results of Table 1 show that the incorporation of correlation effects [26] has little effect on the MESP and PD-ACs of monomers. Thus the SCF results are adequate for the EPIC model calculations.

Nguyen et al. noted [27] that if a high quality basis set is employed then the basis set superposition error (BSSE) is very small. With a BSSE correction, the interaction energy for the complex "a" is less by 0.37 and 0.42 kJ/mol at the SCF and MP2/ 6-31++G(*d,p*) levels, respectively. For $C_3H_8..NH_3$(f) these values are 0.27 and 0.35 kJ/mol. For other structures these values are found to be less than 0.4 kJ/mol.

In the present study, the point charges are placed only on the atom centres of monomers considered in the EPIC model. By employing supplementary non-atom centred point charges [28] quantitatively better results may be obtained. For instance, one may include an additional point charge on the C_3 axis of NH_3 and at the centroid of the C_3H_6 ring.

From a fundamental point of view it is important that MESP is an observable quantity [29, 30], and can be easily enumerated in theoretical models. As a consequence of this, various electrostatic models have been investigated in the last 50 years. For example, a point-charge electrostatic model has been employed for the interaction between water molecules [31]. A similar type of model is found useful for understanding the directionality of the H-bond [1, 32]. A lock and key electrostatic model has been used for the study of crystal packing and protein-ligand complexes [32]. A model for intermolecular angles and energy has been employed for the investigation of B..HX type complexes [33], etc. Electrostatic models are capable of predicting structures and energies [33] that agree well with those from a full SCF treatment and with experimental values. Earlier studies suggest that electrostatics is sufficient for the investigation of $C_3H_6..NH_3$ and $C_3H_8..NH_3$ complexes. Our model is a further attempt in this direction, the difference being that complete electrostatic information furnished by MESP and its topography is employed here, and not the partial model offered by multipoles, etc.

The quantum mechanical theory of H-bonding shows that interaction energy can be partitioned into electrostatic, delocalization, dispersion and repulsive terms. Various methods have been investigated for the decomposition of energy [34]. To find the electrostatic contribution in the interaction energy, the Morokuma analysis [2] was carried out. The results of this analysis presented in Table 3, show that the electrostatic contribution is comparable to that of charge transfer at the 6-31G(*d,p*) basis. However, the electrostatic contribution is the most dominant one at the 6-31++G(*d,p*) basis. This analysis and the aforementioned success of electrostatic-based models suggests that such models can be fruitfully applied for the study of rather weakly bound

Table 3. Morokuma analysis for the energy decomposition at the 6-31G(*d*,*p*) (1) and 6-31++G(*d*,*p*) (2) basis set levels. E_{ELEC} and E_{CT} are the electrostatic and charge transfer contributions, respectively. E_{INT} is the interaction energy at the SCF level. (Energies in kJ/mol)

Complex	E_{INT}			E_{ELEC}		E_{CT}	
	Model (1)	SCF (1)	SCF (2)	SCF (1)	SCF (2)	SCF (1)	SCF (2)
a	−8.35	−4.80	−2.43	−2.90	−3.32	−3.07	−0.50
b	−8.17	−4.69	−2.36	−2.77	−3.11	−3.11	−0.46
c	−6.46	−4.25	−2.23	−2.98	−4.16	−2.39	−0.96
d	−6.22	−2.52	−2.02	−2.85	−3.31	−1.43	−0.71
e	−4.56	−2.44	−2.08	−2.73	−3.15	−1.30	−0.63
f	−2.63	−3.82	−1.17	−1.34	−1.76	−2.23	−0.51
g	−2.51	−3.60	−0.87	−0.21	−1.89	−2.52	−0.71
h	−0.61	−1.77	−0.72	−0.08	−1.55	−0.42	−0.55
i	−1.25	−0.85	+0.16	−0.21	−0.21	−2.43	−0.13
j	−1.46	−0.30	+0.07	−1.55	−0.21	−3.02	−0.13

complexes as illustrated by ammonia...propane and ammonia...cyclopropane complexes.

4 Conclusions

MESP topography and a simple electrostatic model viz. EPIC, have been used for exploring the structure and energies of cyclopropane..ammonia and propane..ammonia complexes. MESP topography offers valuable guidelines for the search of stationary points as illustrated by the present study. The most stable structure is found in the vicinity of the most negative-valued MESP CP of either of the interacting molecules. Further, the EPIC model is capable of yielding good estimates of the interaction energy and the orientation of structure. These model structures can be used as guess points for subsequent full ab initio treatment.

Our high-level molecular orbital (MO) calculations provide strong support for the formation of a weak and non-conventional complex of cyclopropane-ammonia which has been found experimentally [9]. In this complex the ammonia umbrella is pointed up, stacked onto the ring of cyclopropane and the hydrogen atoms prefer a staggered arrangement, and the whole complex is found to be stable. The other two umbrella-up structures, viz. eclipsed and H-bonded, have comparable stability. However, the structures with ammonia around the plane of cyclopropane are found to be less stable. Various possible structures are found for the propane-ammonia complex. Here also, the ammonia umbrella-up structure is found to more stable than others. These complexes are found to be somewhat less stable than the cyclopropane-ammonia ones.

The electrostatic interaction energies are found to be in the range of ab initio energies: the EPIC energy value lies typically between the corresponding SCF and MP2 ones. The correlation between the MESP topography of monomers and their intermolecular complexation shows that the location and the value of MESP at the CP of the monomers offers useful pointers about the structure and energetics of the complex.

The SCF docking interaction energy and distances are almost equal to that for a fully optimized ab initio one. It is an indication that the internal geometry of the propane or ammonia does not change significantly after full optimization. The inclusion of the electron correlation effect in the calculation almost doubles the SCF interaction energy and shortens the intermolecular distance. However, the rank orders of the SCF and MP2 optimized energies are not significantly different.

The results of Morokuma energy decomposition analysis show that the electrostatic term is dominant. However, it is observed that the analysis is dependent on the basis set. BSSE correction is found to be very small with a good quality basis set. The interaction energies are found to be numerically less with the 6-31++G(*d*,*p*) basis set compared to the 6-31G(*d*,*p*) basis set.

In summary, valuable hints on geometries and energetics are offered by the electrostatic model for explaining weak intermolecular complexes. Subsequent high-level theoretical treatments are certainly possible. However, they are greatly assisted by the simple EPIC predictions.

Acknowledgements. Support from the Council of Scientific and Industrial Research (CSIR), New Delhi, in the form of project [01 (1430)/96/EMR-II] is gratefully acknowledged.

References

1. Legon AC, Millen DJ (1987) Chem Soc Rev 16:467
2. Umeyama H, Morokuma K (1977) J Am Chem Soc 99:1316
3. Buckingham AD, Fowler PW (1983) J Chem Phys 79:6426
4. Alhambra C, Luque FJ, Orozco M (1995) J Phys Chem 99:3084
5. Dykstra CE (1993) Chem Rev 93:2339
6. Gadre SR, Bhadane PK, Pundlik SS, Pingale SS (1996) In: Murray J, Sen KD (eds) Molecular electrostatic potential: concepts and applications. Elsevier, pp 219
7. Andrews AM, Hillig KW II, Kuczkowski RL (1992) J Chem Phys 96:1784 and references therein
8. Coulson CA, Moffitt WE (1949) Philos Mag 40:179
9. Forest SE, Kuczkowski RL (1994) Chem Phys Lett 218:353
10. Gadre SR, Kulkarni SA, Suresh CH, Shrivastava IH (1995) Chem Phys Lett 239:273
11. Politzer P, Murray JS (1991) Rev Comput Chem 2:273
12. Politzer P, Truhlar DG (eds) (1981) Chemical applications of atomic and molecular electrostatic potentials. Plenum, New York
13. The package INDPROP developed by Gadre et al. see, Shirsat RN, Bapat SV, Gadre SR (1992) Chem Phys Lett 200:373
14. Bader RFW (1990) Atoms in molecules: A quantum theory. Clarendon, Oxford
15. Pauling L (1960) The nature of the chemical bond and the structure of molecules and crystals: An introduction to modern structural chemistry. Cornell, New York
16. Shirsat RN, Limaye AC, Gadre SR (1993) J Comput Chem 14:445
17. Schmidt MW, Baldridge KK, Boatz JA, Elbert ST, Gordon MS, Jensen JH, Koseki S, Matsunaga N, Nguyen KA, Su SJ, Windus TL, Dupuis M, Montgomery JA (1993) J Comput Chem 14:1347
18. The FORTRAN program performing charge fitting to molecular electrostatic potentials is available from Chipot C, Universite de Nancy, France. We are thankful to Dr. C. Chipot for supplying us this code. See also, Chipot C, Angyan JG, Ferenczy GG, Scheraga HA (1993) J Phys Chem 97:6628
19. Ruoff RS, Emilsson T, Jaman AI, Germann TC, Gutowsky HS (1992) J Chem Phys 96:3441

20. Schulz B, Botschwina P (1995) Chem Phys Lett 243:378
21. Rodham DA, Suzuki S, Suenram RD, Lovas FJ, Dasgupta S, Goddard WA III, Blake GA (1993) Nature 362:735
22. Stone AJ (1981) Chem Phys Lett 83:233
23. Spoliti M, Bencivenni L, Ramondo F (1994) J Mol Struct (Theochem) 303:185
24. McDowell SAC, Buckingham AD (1991) Chem Phys Lett 182:551
25. Lin Z, Bytheway I (1995) Chem Phys Lett 240:541
26. Kulkarni SA (1996) Chem Phys Lett 254:268
27. Nguyen MT, Coussens B, Vanquickenborne LG, Gerber S, Huber H (1990) Chem Phys Lett 167:227
28. Bonaccorsi R, Petrongolo C, Scrocco E, Tomasi J (1971) Theor Chim Acta 20:381
29. Brinck T, Murray JS, Politzer P (1992) Int J Quantum Chem Symp 19:57
30. Cummins PL, Gready JE (1990) Chem Phys Lett 174:355
31. Bernal JD, Fowler RH (1933) J Chem Phys 1:515
32. Naray-Szabo G, Ferenczy GG (1995) Chem Rev 95:829
33. Rendell APL, Backsay GB, Hush NS (1985) Chem Phys Lett 117:400
34. Tomasi J, Mennucci B, Cammi R (1996) In: Murray J, Sen KD (eds.) Molecular electrostatic potential: concepts and applications. Elsevier p1