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The molecular structure of the $(NCCN)_2$ and $(PCCP)_2$ van der Waals dimers

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The stationary points on the potential energy surfaces of the $(NCCN)_2$ and $(PCCP)_2$ van der Waals homodimers have been examined at the *ab initio* Hartree–Fock level of theory employing a 4-31G basis set. Only a T-shaped C_{2v} stable minimum energy structure was found for the $(NCCN)_2$ dimer, while two energetically very similar stable minima, exhibiting near T-shaped C_s and slipped-parallel C_{2h} spatial arrangements, were predicted for the $(PCCP)_2$ dimer. Our predictions for the $(NCCN)_2$ complex are in agreement with a recent gas phase spectroscopic study. No experimental gas phase study seems to have been reported for the $(PCCP)_2$ dimer, and our results indicate that an equilibrium between a near T-shaped and a parallel form is likely to occur. The implications of including electron correlation effects and higher polarized/diffuse functions are discussed.

1. Introduction

Over the past few years there has been a growing interest in the structure, energetics and spectroscopic properties of weakly bound molecular complexes. The existence of these so called van der Walls (vdW) dimers was first observed directly by electron diffraction [1–3] and mass spectrometry [4–5]. The main spectroscopic techniques which have been used to study the potential energy functions of these species are high-resolution ultraviolet and infrared spectroscopy, and molecular beam electric resonance spectroscopy in the microwave and radiofrequency regions. The methods give information about the vibrational and rotational energy levels of the dimer, and it is through this detail that information about the intermolecular potential function is obtained.

Great advances in infrared and microwave spectroscopy allied to continuous progress in the theoretical approaches and combined with the development of more powerful computers, have provided us with a considerable amount of information regarding the molecular properties and interaction energies of vdW complexes. Reviews of the present status of experimental and theoretical fields can be found, respectively, in references [6–9] and [10–16]. Although providing accurate data of molecular structure, energies and electrical properties of weakly bound gas-phase dimers, in some cases the experimental results alone are insufficient for the unambiguous determination of the geometry of the minimum energy structure present on the multidimensional and most frequently multivalued potential energy surface (PES). In such situations the theoretical calculations have proved to have a valuable role to play. The following molecular complexes serve as an example of the relevance

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of such theoretical studies: $(HF)_2$ [17–21], HCN ... HF [22, 23], $(HCCH)_2$ [24], CO ... HF [25], HF ... ClF [26], C_2H_2 ... CO [27, 28], $(H_2O)_2$ [29, 30], $(NH_3)_2$ [29, 31], B ... Cl dimers (B is CO, HCN, H_2O, H_2S, C_2H_2, C_2H_4, NH_3, PH_3, or CH_3CN) [32], $(HCN)_2HF$ and $HCN(HF)_2$ trimeric species [33], H_3SiOH ... H_2 [34], $(HCP)_2$ [35], N_2 ... ClF [36] and benzene ... ClF [37].

The main conclusion that emerges from these series of calculations is that the Hartree–Fock (HF) self-consistent field (SCF) method employing moderate/extended basis sets yields results that often are qualitatively correct. However, it is found that, in order to obtain reliable stabilization energies, intermolecular geometrical parameters and harmonic frequencies, an appropriate treatment of the electron correlation employing extended basis sets containing both higher polarized and diffuse functions is generally required. The most straightforward way to include electron correlation is through second-order Møller–Plesset perturbation theory (MP2) [38]. Accurate predictions of geometries and harmonic frequencies by MP2 are possible with sufficiently large basis sets [39]. Nevertheless the overall trend in the calculated molecular properties can be considered to be satisfactorily represented at the HF level of theory.

The weakly bound dimers originating from the interaction between two non-polar monomeric species are known to be bound basically by the London dispersion forces [40], since the electrostatic contribution to the stabilization energy is the small quadrupole–quadrupole interaction; so this is a case where electron correlation plays a major role. It is opportune to say that the dispersion energy contribution to the total intermolecular interaction energy can be considered to be identical to the intersystem correlation energy for large distances [41, 42]. An example of a dimer of this type is the $(Cl_2)_2$ homodimer, where the global minimum near-T-shaped structure is stabilized by 6·91 kJ mol^{-1} at the correlated MP2 [38] level of theory employing the 6-31$^+$G* basis set (which contains both polarization and sp diffuse functions), while at the HF/6-31$^+$G* level it is predicted to be bound by just 0·782 kJ mol^{-1} [43]. In this case it is seen that the binding energy increased by a factor about 9 when electron correlation was taken into account. Also, the intermolecular geometrical parameters were found to be affected by electron correlation. However, it is interesting to point out that the MP2 and HF geometries of the stationary points located on the PES for the $(Cl_2)_2$ dimer, i.e., T-shaped parallel or linear structures, agreed within less than 20° for the intermolecular bond angles. Also, the intermolecular distances are about 25% longer at the HF level, which is a well understood expected result. From these results the molecular geometry can be seen to be satisfactorily predicted at the HF level of theory, in the sense that the rough spatial orientation of the monomer subunits after complexation is correctly predicted.

The effect of electron correlation on the calculated harmonic frequencies (necessary for the characterization of the stationary points on the PES) for weakly bound molecular complexes has been addressed in various articles [29, 35, 43–45]. The general conclusion arising from these studies is that the low frequency intermolecular modes are shifted towards larger values while the corresponding high-frequency intramolecular modes are considerably smaller when evaluated at the MP2 correlated level of theory. The important issue originating from this is that a transition state structure exhibiting a very small imaginary frequency may well be a true minimum energy structure (all frequencies are positive) when electron correlation effects are taken into account. This fact can be explained in the light of the inadequacy of the HF method for describing accurately the curvature of the PES around the minimum region.

Bearing these points in mind, it can be said regarding *ab initio* calculations involving weakly bound vdW homodimers that the HF method would almost certainly underestimate binding energies, predict unrealistically small intermolecular frequencies, exaggerate intermolecular distances, and produce reasonable intermolecular bond angles. So, once the size of a given molecular system is prohibitive for a MP2 type calculation the HF method, if used with care, may provide useful information about the vdW dimer.

One of the most interesting classes of vdW dimer comprises those made up of two nonpolar species. Complexes involving monomers like HCCH, NCCN and PCCP are interesting because they are the simplest molecules whose first non-vanishing electrostatic multipole is their electric quadrupole moment. The ground-state intermolecular potential is due to interactions between closed shell molecules, and so quadrupolar interactions and dispersive attractive forces are expected to take part in the energetic balance determining the intermolecular potential energy function. Parallel and T-shaped geometrical arrangements are the probable candidates for the observed minimum structure.

The C_2N_2 and HCP molecules are among the several species which have been observed in the interstellar medium. This fact certainly makes an investigation of the occurrence of dimeric species involving C≡N and C≡P bonds a relevant task once the complex chemistry and dynamics of the upper atmosphere exist in a low-pressure, low-temperature medium where vdW complexes can exert maximum influence. The chemistry of molecular species containing P≡X triple bonds has been reviewed recently [46], where experimental procedures for obtaining compounds like H—C≡P, P≡C—C≡P, N≡C-C≡P, H—C≡P—C≡P and N≡C – C≡C—C≡P have been discussed. The C_2N_2 isomers [47] and the $(HCP)_2$ dimer [35] have been examined previously at the *ab initio* level of theory, and in this paper we are therefore applying the HF method to the investigation of the stationary points on the PES for the $(NCCN)_2$ and $(PCCP)_2$ vdW homodimers. While spectroscopic gas phase results for the $(NCCN)_2$ dimer have been published recently [48], we are not aware of any experimental or theoretical study carried out for the $(PCCP)_2$ homodimer. The authors hope that the present study can be useful for spectroscopists working in the field of weak molecular interactions in the gas phase.

2. Calculations

The initial symmetrical linear ($C_{\infty v}$), T-shaped (C_{2v}) and parallel (D_{2h}) configurations given by figure 1 were used as starting points for the geometry optimization procedure in the search for stationary points on the PES of the $(NCCN)_2$ and $(PCCP)_2$ homodimers. This procedure has been applied successfully for the $CO_2 \ldots HCCH$ [49] and $CO_2 \ldots HCN$ [50] complexes. A pointwise calculation of the PES that could lead to the determination of the energy barriers for conformational interconversion or tunnelling motion, as reported for the HF...ClF [51], $N_2 \ldots ClF$ [45] and $HF \ldots Cl_2$ [52] binary complexes, has not been carried out due to the shortage of computer resources. Full symmetry-unconstrained geometry optimization for each of the three trial structures was performed, with the intermolecular out-of-plane dihedral angle being compelled to be zero. By doing this, non-planar spatial arrangements such as a crossed D_{2d} symmetrical structure, predicted for the $(N_2)_2$ homodimer [53], have not been considered in the present work. Nevertheless, the fact that the experimentally observed [48] structure of the $(NCCN)_2$ vdW dimer

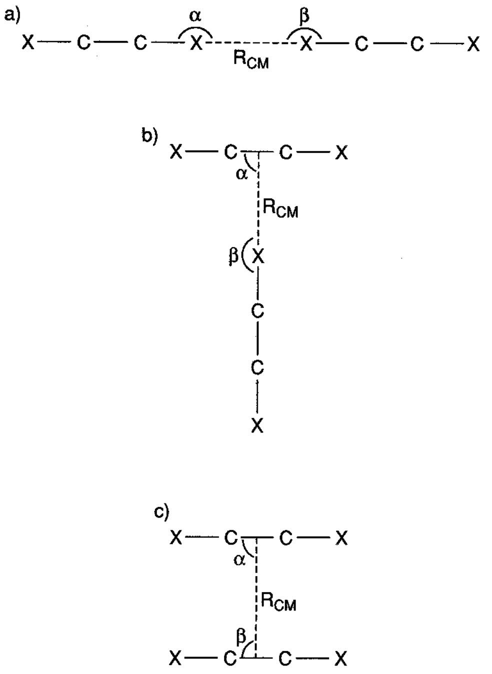

Figure 1. Initial configurations used as a starting point for the geometry optimization procedure in the search for stationary points of the potential energy surface for the $(XCCX)_2$ homodimers: X = N or P.

is planar T-shaped (C_{2v}) is an indication that the planarity assumption is valid. The calculations were carried out at the HF SCF level of theory employing the split valence 4-31G [54] with the *ab initio* molecular orbital (MO) package Gaussian-86 [55].

3. Results and discussions

The stationary points located on the PES for the $(NCCN)_2$ and $(PCCP)_2$ homodimers are given in figure 2 with the values of the intermolecular geometrical parameters R, α and β being quoted also. The linear $(PCCP)_2$ structure optimized to a near-T-shaped configuration, and so only two stationary points for the $(PCCP)_2$ dimer survived when full geometry optimization took place in the six-dimensional configuration space. Table 1 contains a summary of the HF/4-31G SCF calculations on both dimers and the respective monomers, and table 2 gives the intermolecular harmonic frequencies which are needed for the characterization of the stationary points. It is seen that the slipped-parallel $(NCCN)_2$ homodimer is a first-order transition state structure while the linear dimer is a fourth-order transition state structure which is a stationary point of no interest at all. The near-T-shaped $(PCCP)_2$ dimer exhibits one very small negative frequency ($\omega_1 = -2{\cdot}79\ \mathrm{cm}^{-1}$) value, and so it should be classified as a first-order transition state structure, that could be on the way for the interconversion between two equivalent parallel configurations. However it has been found that the HF/4-31G approach generally underestimates intermolecular frequencies [29, 35, 43–45] and so it is believed that the near-T-shaped $(PCP)_2$ dimer

Table 1. HF/4-31G geometrical parameters (defined in figure 1), rotational constants (A, B and C), dipole moments (P_e), total energies (E_{tot}) and stabilization energies (ΔE) for the monomeric and dimeric species.

	N–C–C–N	$(NCCN)_2$ T-shaped	$(NCCN)_2$ Slipped-parallel	$(NCCN)_2$ Linear
Symmetry		C_{2v}	C_{2h}	$C_{\infty v}$
$r_{C–N}$/Å	1·140	1·140	1·140	1·178
$r_{C–C}$/Å	1·372	1·373	1·373	1·322
θ(N–C–C–)/deg	90·0	90·0	90·0	90·0
R_{CM}/Å		5·106 [4·987][a]	5·064	4·862
α/deg		89·9	43·4	179·9
β/deg		179·9	43·4	179·9
P_e/D[b]		0·326 [0·420][a]	0·0	0·007
E_{tot}/E_h[c]	−184·309 605	−368·621 628	−368·620 916	−368·381 839
ΔE/kJ mol^{-1}		−6·35	−4·48	623
ΔE^{ZERO}/kJ mol^{-1}		1·06	0·77	
ΔE^{BSSE}/kJ mol^{-1}		1·99	1·89	
A/cm^{-1}		0·160 95 [0·147 00][a]	0·203 03	
B/cm^{-1}	0·160 94	0·021 54 [0·022 54][a]	0·021 25	0·020 43
C/cm^{-1}	0·160 94	0·019 00 [0·019 57][a]	0·019 24	0·020 43

	P–C–C–P	$(PCCP)_2$ Near-T-shaped	$(PCCP)_2$ Slipped-parallel
Symmetry		C_s	C_{2h}
$r_{C–P}$/Å	1·551	1·551	1·551
$r_{C–C}$/Å	1·345	1·345	1·345
θ(P–C–C–)/deg	90·0	90·0	90·0
R_{CM}/Å		5·892	4·566
α/deg		80·9	115·5
β/deg		152·2	64·5
P_e/D[b]		0·162	0·0
E_{TOT}/E_H[c]	−756·176 353	−1512·353 187	−1512·353 222
ΔE/kJ mol^{-1}		−1·26	−1·36
ΔE^{ZERO}/kJ mol^{-1}		0·32	0·44
ΔE^{BSSE}/kJ mol^{-1}		2·70	4·40
A/cm^{-1}		0·047 54	0·040 61
B/cm^{-1}	0·053 17	0·009 51	0·015 12
C/cm^{-1}	0·053 17	0·007 93	0·011 02

[a] Experimental value from reference [48].
[b] D = debye ≈ 3·335 64 × 10^{-30} C m.
[c] E_h = hartree ≈ 4·359 75 × 10^{-18} J.

could be a true minimum energy structure (all frequencies positive) if a large basis set and/or an electron correlation treatment is used.

From table 1 it can be seen that there is satisfactory agreement between the HF/4-31G and the experimental results [48] reported for the T-shaped $(NCCN)_2$ homodimer. At the HF/4-31G level the intermolecular distance R is only 2% longer than the experimental value and the rotational constants are within 3–9% of the experimental figures. So the geometry can be said to be very satisfactorily predicted

Table 2. HF/4-31G intermolecular harmonic frequencies (ω) for the stationary points located on PES for the $(NCCN)_2$ and $(PCCP)_2$ dimers.

$(NCCN)_2$			
T-shaped (C_{2v})		Slipped-parallel (C_{2h})	Linear ($C_{\infty v}$)
Frequency	Mode description	Frequency	Frequency
ω_1 13·4	Bend in-plane	ω_1 −14·1	ω_1 −640
ω_2 24·2	Bend out-of-plane	ω_2 16·5	ω_1 −486
ω_3 50·7	vdW stretching	ω_3 20·55	ω_3 −174
ω_4 59·5	Bend in-plane	ω_4 69·83	ω_4 −48·6

$(PCCP)_2$			
Near-T-shaped (C_s)		Slipped-parallel (C_{2h})	
Frequency	Mode description	Frequency	Mode description
ω_1 −2·79	Bend in-plane	ω_1 7·13	Bend out-of-plane
ω_2 6·44	Bend out-of-plane	ω_2 17·4	Bend in-plane
ω_3 9·91	Bend in-plane	ω_3 17·9	Bend in-plane
ω_4 31·5	vdW stretching	ω_4 37·6	vdW stretching

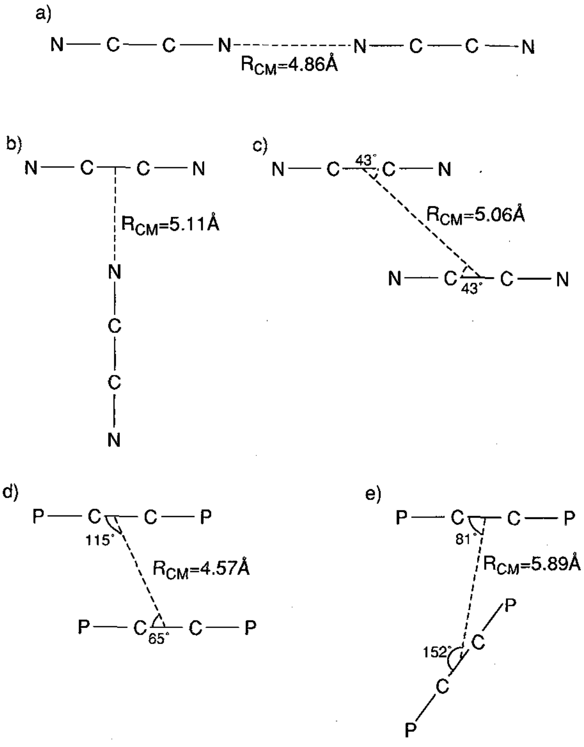

Figure 2. Stationary points found on the PES for the $(NCCN)_2$ and $(PCCP)_2$ vdW dimers: (a) $(NCCN)_2$ linear $C_{\infty v}$; (b) $(NCCN)_2$ T-shaped; (c) $(NCCN)_2$ slipped-parallel C_{2h}; (d) $(PCCP)_2$ slipped-parallel C_{2h}; (e) $(PCCP)_2$ near-T-shaped.

at the HF level of theory. The dipole moment is well known to be a more sensitive molecular property to be calculated by *ab initio* methods, and the deviation of 22% from the experimental reported value is not a big surprise. The problems of evaluating theoretically the molecular dipole moment have been discussed in detail in [56]. From the above comparisons it can be stated that the HF/4-31G geometrical parameters reported here for the $(PCCP)_2$ dimer should be viewed as satisfactory and so it may guide the experimentalists in the assignment of the equilibrium structure through rotational spectroscopy. The fact that theory predicts the possibility of only a T-shaped structure for the $(NCCN)_2$ dimer in total agreement with the experimental findings [48], is additional support for the validity of the HF/4-31G approach for the determination of the molecular structure of such weakly bound vdW complexes.

The PCCP subunit can form two stable dimers energetically very close, i.e., a near-T-shaped C_s structure and a slipped-parallel C_{2h} configuration, which are depicted in figure 2. The C_{2h} structure is predicted to be only 0·1 kJ mol^{-1} more stable than the C_s at the HF/4-31G level. However, it is seen that zero-point energy (ZPE) corrections can invert the energetic order. Also, if electron correlation effects are taken into account, the global minimum energy structures on the PES can be of either C_s or C_{2h} symmetry. The basis set superposition error (BSSE) correction evaluated using the counterpoise method [61] is seen to be quite substantial for the 4-31G basis set, particularly for the $(PCCP)_2$ homodimer. The BSSE counterpoise correction method has been addressed many times in the literature [16, 21, 29, 42, 62–65]. In the light of the results reported in these studies it appears that the counter poise approach does overestimate the BSSE correction. Like the $(Cl_2)_2$ homodimers [43], the $(PCCP)_2$ dimers constitute an example where electron correlation plays a fundamental role, and so it can account for practically the whole of the binding of the dimeric species. The considerations made above may provide an explanation for the C_s and C_{2h} $(PCCP)_2$ homodimers being predicted to be much less stable than the C_{2v} $(NCCN)_2$ dimer at the HF/4-31G level of theory. These weakly bound vdW complexes are bound predominantly through dispersion forces and, although the HF method can produce a satisfactory molecular structure, it provides poor binding energies and so cannot be relied on for the determination of vdW energies.

Table 3 contains electric quadrupole moments, electric dipole polarizabilities and first-ionization potentials for the isolated monomers. They are given basically to supplement the experimental data reported for these species, since they are important quantities which can be used in the determination of intermolecular interaction energies. The performance of the *ab initio* methods regarding the determination of molecular properties has been reviewed in [59].

For the interaction between non-polar linear molecules the electric quadrupole moment is responsible for the major electrostatic contribution to the total interaction energy. The electrostatic part of the long-range interaction energy U_{elec} is proportional to Q^2/R_{CM}^5 [40, 41], since the dipole type interactions are absent. The dispersion contribution to the long range interaction energy is given essentially by $U_{\mathrm{disp}} = C_6/R_{\mathrm{CM}}^6$, where C_6 is the dispersion coefficient which may be evaluated using the dipole polarizabily and ionization potential [40, 41]. So the long-range interaction energy between two molecules A and B may be partitioned into two main contributions, i.e.

$$\Delta E = U_{\mathrm{elec}} + U_{\mathrm{disp}}$$

Table 3. Electric quadrupole moments Q_{aa} (in principal axis coordinates), mean dipole polarizabilities α, and first-ionization potentials E_I, for some non-polar diatomic molecules.

Method	Molecule	Q_{aa} 10^{40}/C m^2	α 10^{40}/C^2 m^2 J^{-1}	E_I/eV
HF/4-31G	PCCP	11·0018	9·5936	−8·7386
HF/4-31G	NCCN	−36·0423	3·8553	−13·6251
HF/6-31$^+$G*	NCCN	−32·4255 (−20·6808)[a]	4·4964 [5·013][a]	−13·7976
HF/6-31$^+$G*	Cl_2	9·0949	3·4439	−12·2324
HF/6-31$^+$G*	N_2	−4·9554 [−4·67][b]	1·5984 [1·97][c]	−17·0176
UHF/6-31$^+$G*	O_2	−1·6161 [−1·30][b]	1·4690 [1·78][d]	−14·8090

[a] Experimental value taken from [48].
[b] Experimental value from [58].
[c] Experimental value from [59].
[d] Experimental value from [57].

with the expressions for U_{elec} and U_{disp} given by [40, 41]

$$U_{\text{elec}} = \frac{3}{4}\frac{Q_A Q_B}{4\pi\varepsilon_0}\frac{1}{R_{AB}^5}\begin{pmatrix} 1 - 5\cos^2\theta_A - 5\cos^2\theta_B + 17\cos^2\theta_A\cos^2\theta_B \\ +2\sin^2\theta_A\sin^2\theta_B\cos^2\phi \\ -16\sin\theta_A\sin\theta_B\cos\theta_A\cos\theta_B\cos\phi \end{pmatrix}$$

$$U_{\text{disp}} = C_6/R_{AB}^6,$$

where the intermolecular angles are defined by the line connecting the centre of mass of the linear subsystems A and B as shown in figure 3. The coefficient C_6 can be estimated in a simple way by using the London approximation [40, 41]

$$C_6 = \frac{3}{4}\frac{\alpha_A\alpha_B}{(4\pi\varepsilon_0)^2}\frac{E_A E_B}{(E_A + E_B)},$$

where ε_0 is the permittivity of free space and α_A, α_B and E_A, E_B are, respectively, the dipole polarizabilities and the ionization energies of the isolated monomers.

Table 4 contains a summary of interaction energy results for a series of dimeric species evaluated with both the long range partitioned method (using the monomer molecular properties given by table 3 and R_{AB} values from table 1) and the *ab initio* supermolecule approach. The energy data for the $(NCCN)_2$ and $(PCCP)_2$ dimers, evaluated with the supermolecule method, where taken from table 1. The relative importance of the dispersion energy for each dimeric species can then be assessed.

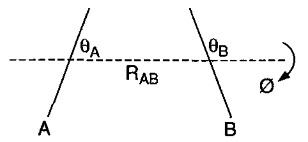

Figure 3. Coordinate system used for describing the intermolecular potential.

Table 4. Distinct contributions to the total interaction energy (ΔE_{tot}) for some weakly bound dimers. U_{elec} and U_{disp} are respectively the long range electrostatic and dispersion energies, and C_6 is the dispersion coefficient.

		ΔE: long range[a] Partitioned method		ΔE: *ab initio*[b] Supermolecule method			Dispersion[c] coefficient
		U_{elec}	U_{disp}	ΔE^{HF}	ΔE^{HF}_{BSSE}	ΔE^{MP2}	$-C_6 \times 10^{79}$
Basis set	Dimer	kJ mol^{-1}	kJ mol^{-1}	kJ mol^{-1}	kJ mol^{-1}	kJ mol^{-1}	J m^6
4-31G	$(NCCN)_2$:T-shaped	−6·078	−0·668	−6·35	1·99		196·6
6-31$^+$G*	$(NCCN)_2$:T-shaped	−4·117	−0·743	−3·89			270·8
		[−4·64][d]	[−1·13][e]				
4-31G	$(NCCN)_2$:Parallel	−4·882	−0·702	−4·48			196·6
4-31G	$(PCCP)_2$:T-shaped	−0·390	−1·124	−1·26	2·70		780·7
4-31G	$(PCCP)_2$:Parallel	−0·245	−5·188	−1·36	4·40		780·7
6-31$^+$G*	$(Cl_2)_2$:T-shaped	−0·240	−0·270	−0·782	0·04	−6·13	140·8
6-31$^+$G*	$(Cl_2)_2$:Parallel	0·263	−0·426	−0·364	—	−4·97	140·8
6-31$^+$G*	$(Cl_2)_2$:T-shaped[f]	−0·230	−0·868	—	—	—	
6-31$^+$G*	$(Cl_2)_2$:Parallel[f]	0·066	−1·936	—	—	—	
6-31$^+$G*	$N_2 \cdots O_2$:Linear	0·142	−0·132	−0·896	1·15	−2·84	18·05
6-31$^+$G*	$N_2 \cdots O_2$:T-shaped	−0·067	−0·124	−0·616	0·64	−2·66	18·05
6-31$^+$G*	$N_2 \cdots O_2$:Parallel	0·078	−0·210	−0·546	0·72	−2·81	18·05
							[63·4][h]
6-31$^+$G*	$N_2 \cdots O_2$:Linear[i]	0·160	−0·153	—	—	—	
6-31$^+$G*	$N_2 \cdots O_2$:T-shaped[i]	−0·135	−0·286	—	—	—	
6-31$^+$G*	$N_2 \cdots O_2$:Parallel[i]	0·212	−0·692	—	—	—	
6:31$^+$G*	$(N_2)_2$:Crossed-D_{2d}	0·201[j]	−1·481[j]	—	—	—	42·21
			[−1·46][g]	—	—	—	
6-31$^+$G*	$(N_2)_2$:Slipped-C_{2h}	0·071[j]	−1·093[j]	—	—	—	42·21
			[−1·29][g]				
6-31$^+$G*	$(O_2)_2$:Parallel:D_{2h}	0·069[k]	−1·188[k]	—	—	—	31·02
							[56·0][h]

[a] The references for the geometrical parameters were, respectively, $(Cl_2)_2$ [43], $N_2 \ldots O_2$ [60], $(N_2)_2$ [53] and $(O_2)_2$ [57].

[b] The energy values were $(Cl_2)_2$ [43] and $N_2 \ldots O_2$ [60].

[c] Evaluated using the London's formula [40, 41] and the data from table 3.

[d] Experimental value from [48].

[e] Evaluated using the experimental value of α from reference [48].

[f] Evaluated using the MP2/6-31$^+$G* geometrical parameters.

[g] Experimental ΔE value from [53].

[h] Experimental value taken from [57].

[i] Evauated using the UMP2/6-31$^+$G* geometry.

[j] R_{ab} value taken from [53]. [k] R_{AB} value taken from [57].

As has been pointed out earlier by Pople [66], since the HF method takes no account of dispersion forces, which depend intrinsically on correlation between electrons in separate molecules, it is likely to be more successful for interaction between polar systems where electrostatic interactions dominate (for example hydrogen bonding) than for true vdW species whose weaker interaction potentials are dominated by dispersion forces. Perhaps the simplest size-consistent (the intermolecular potential energy tends to zero as the intermolecular distance tends to infinity) post-Hartree–Fock procedure is Møller–Plesset perturbation theory [38] carried out fully to any order. The second-order theory (MP2) contribution of electron correlation, in the supermolecule approach, for the interaction between the subsystems A and B is

$$\Delta E_{AB}\ (\text{correlation}) = \Delta E^{MP2} = E^{(2)}_{AB} - (E^{(2)}_{A} + E^{(2)}_{B}).$$

Thus, the intermolecular interaction energy can be written as

$$\Delta E = \Delta E^{HF} + \Delta E^{MP2},$$

where ΔE^{HF} encompasses both short range and long range electrostatic parts, while ΔE^{MP2} carries on the dispersion effects. At sufficiently large distances it can be shown that ΔE^{MP2} does include a dispersion force term proportional to R_{AB}^{-6} [66]. Once the vdW distances are large ($\approx$4–5 Å), we may assume that $U_{elec} \approx \Delta E^{HF}$ and $U_{disp} \approx \Delta E^{MP2}$, and then compare the supermolecule calculations with the results from the partitioned method derived here, neglecting the short-range contributions to the interaction energy.

From table 4 it can be seen that the HF/4-31G interaction energy corrected for BSSE of the $(NCCN)_2$ dimer agrees fairly well with the experimental value for U_{elec} reported by Suni *et al.* [48], and also that the HF/6-31$^+$G* value is not so far from the experimental U_{elec} value. Our calculated U_{elec} using the HF/6-31$^+$G* Q_{NCCN} value also correlates well with the experimental result. From these findings it can be concluded that the assumption that $U_{elec} = \Delta E^{HF}$ should be seen as a reasonable one for vdW species. The U_{disp} values calculated with the HF/4-31G and HF/6-31$^+$G* molecular properties from table 3 are seen to be considerably lower than the value estimated using the experimental dipole polarizability from [48]. It can be understood in the light of the smaller α values, calculated at the HF level, compared with experiment. So, considering that the equilibrium R_{AB} values are usually overestimated at the HF level, it may be inferred that the U_{disp} values evaluated with HF monomer molecular properties are generally expected to be underestimated when compared with those derived using experimental values. By comparing the electron correlation correction ΔE^{MP2} values reported for the $(Cl_2)_2$ [43] and $N_2 \ldots O_2$ [60] dimers with the respective U_{disp} results the inference made above can be verified.

In the last column of table 4 the values for the coefficients C_6 are quoted, and it can be seen that our calculated C_6 values are well below the experimental findings and, consequently, our U_{disp} results must be considerably underestimated. Indeed, we have calculated the U_{disp} energy for the $(O_2)_2$ parallel D_{2h} homodimer using the experimental C_6 value of 56×10^{-79} J m^6 from reference [57] and the experimental intermolecular distance $R_{AB} = 3.41$ Å taken from reference [67]. We found a value of $U_{disp} = -2{\cdot}145$ kJ mol^{-1}, which is $\approx$45% higher than the value of $-1{\cdot}188$ kJ mol^{-1} reported in table 4.

The fact that the $(Cl_2)_2$, $N_2 \ldots O_2$, $(N_2)_2$, $(O_2)_2$ and the $(PCCP)_2$ vdW dimers are bound mainly through dispersion forces can be seen clearly from the long-range interaction energy results reported in table 4. The experimental binding energies reported for $(N_2)_2$ in table 4 exhibit a satisfactory correlation with the U_{disp} values, and it may allow us to say that, qualitatively, at least more than 80% of the interaction energy for these dimers originated from the dispersion contribution U_{disp}.

Some of the normal vibrations may be associated with a probable tunnelling motion. The lowest in-plane intermolecular bending mode for the $(NCCN)_2$ T-shaped dimer ($\omega_1 = 13{\cdot}4$ cm^{-1}) implies a tunnelling vibration across a C_{2h} slipped-parallel barrier, as has been hinted at by Suni *et al.* [48]. Similarly, the equivalent in-plane bend mode ($\omega_1 = -2{\cdot}79$ cm^{-1}) of the near-T-shaped $(PCCP)_2$ homodimer may also be associated with a tunnelling through a D_{2h} or C_{2h} barrier. Of the intermolecular normal modes of the C_{2h} slipped-parallel $(PCCP)_2$ dimer the two in-plane bending modes ($\omega_2 = 17{\cdot}4\,cm^{-1}$ and $\omega_3 = 17{\cdot}9\,cm^{-1}$) also indicate a tunnelling vibration across a near-T-shaped barrier. These two modes are practically degenerate and so they represent equivalent vibrations.

Whether a C_s near-T-shaped or C_{2h} (or D_{2h}) barrier will exist for the $(PCCP)_2$ homodimers depends basically on which of the two dimer structures located on the PES is effectively the global minimum energy structure. The level of calculation used in the present study is not sufficiently accurate to ensure that the C_{2h} slipped-parallel $(PCCP)_2$ dimer is indeed the global minimum which should be experimentally observed. Nevertheless, the substantial dispersion energy contribution found for the C_{2h} dimer (see table 4) compared with the C_s is an indication that the C_{2h} spatial arrangement may be the lowest energy structure.

It should be emphasized that in order to study accurately the tunnelling motion in these weakly bound dimers a pointwise calculation of the PES around the tunnelling angle, using a correlated level of theory, as for example MP2/6-31$^+$G*, would be required. The HF/4-31G approach has been shown to yield a tunnelling barrier for the HF ... ClF complex [51] which is less than half of the respective MP2/6-31$^+$G* value.

Suni *et al.* [48] have estimated the relative energies of the C_{2v} T-shaped and a hypothetical C_{2h} slipped-parallel forms of the $(NCCN)_2$ dimers using an electrostatic model, and they found that the C_{2h} dimer would be slightly more stable than the C_{2v} one. However, using a full multipole expansion, the C_{2v} was found to be slightly lower in energy than the C_{2h}. We have calculated the U_{disp} values using the experimental data from reference [48] and we found that the dispersion effects favour a C_{2h} structure. These results show that a simple long range partitioned method which takes no account of the anisotropy of the interaction potential may be inadequate for predicting relative stabilities of isomeric forms of vdW dimers. Once deviations from spherical symmetric potentials are taken into account we expect that the C_{2v} $(NCCN)_2$ configuration would be predicted to be the lowest energy structure. Nevertheless, the U_{disp} values calculated with London's formula can be used to assess the dispersion energy contribution to the total interaction energy relative to the electrostatic counterpart. For the determination of molecular structure and energetics of stationary points the *ab initio* methods in conjunction with gradient techniques, needed by geometry optimization procedures, have to be used. Our HF/4-31G calculations reveal that a C_{2h} $(NCCN)_2$ transition state structure does exist (see table 1), and it is $1{\cdot}87\,kJ\,mol^{-1}$ ($156\,cm^{-1}$) less stable than the experimentally observed T-shaped structure. So, a barrier of $156\,cm^{-1}$ for tunnelling motion is predicted for the T-shaped $(NCCN)_2$ homodimer at the HF/4-31G level of theory. This tunnelling barrier should be seen in the light of the HF/4-31G approach used, since an appropriate treatment of electron correlation employing extended basis sets is required in order to obtain reliable energy values.

4. Conclusions

The molecular structure of the $(NCCN)_2$ and $(PCCP)_2$ vdW homodimers has been investigated at the HF level employing a 4-31G basis set. Only a C_{2v} T-shaped minimum energy structure was predicted for the $(NCCN)_2$ dimer in agreement with the experimental findings [48]; also, the intermolecular distance and rotational constants are in satisfactory agreement with the molecular beam electric resonance results reported by Suni *et al.* [48]. The interaction energy values evaluated with the long range partitioned method and the HF supermolecule approach agree relatively well with the experimental results reported for the T-shaped $(NCCN)_2$ dimer.

The PES for the $(PCCP)_2$ homodimer exhibited two stable minimum energy structures: a C_s near-T-shaped and a C_{2h} slipped-parallel spatial arrangement. The results for the $(PCCP)_2$ dimers revealed that, in contrast to the $(NCCN)_2$ complexes, they are bound mainly through dispersion forces. The dispersion energy contribution to the total interaction energy, i.e., U_{disp}, indicated that the C_{2h} $(PCCP)_2$ dimer may be more stable than the C_s. However, the U_{disp} values as calculated in the present study may be more appropriate for determining the dispersion contribution to the interaction energy rather than the relative stability of isomeric forms of a vdW dimer. A further more sophisticated *ab initio* study including electron correlation at the MP2/6-31$^+$G* level, as reported for the $(Cl_2)_2$ homodimers [43], would be highly desirable in order to establish unambiguously the global minimum energy structure on the PES for the $(PCCP)_2$ vdW homodimers.

In spite of the limitations of the Hartree–Fock method for dealing with weakly bound vdW systems, the present study shows that the stable minimum energy structures can still be located on the PES by applying the HF approach. The probable minima can be identified and the approximate binding energies be determined. However, an accurate prediction of relative stablization energies, and therefore the assignment of the global minimum, would require an adequate treatment of electron correlation.

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