

Energetic, Structural, and Vibrational Properties of 4,4'-Methylenediphenyl Diisocyanate with Relevance for Adhesion

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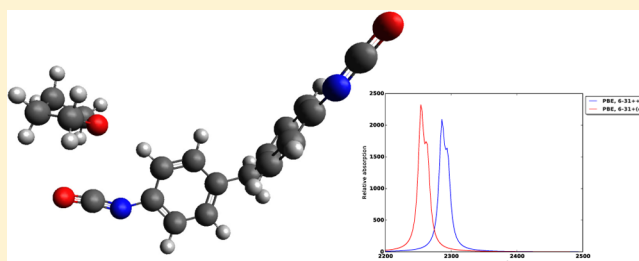
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ABSTRACT: Through a polymerization process, the monomer 4,4'-methylenediphenyl diisocyanate can participate in glueing, whereby strong covalent bonds between the monomer and the substrates that will be glued have to be formed. In the present work, we use density functional theory (DFT) calculations to study a group of properties that are important for the initial steps of this process and for its experimental characterization. We focus on energetic and structural properties of a single monomer of 4,4'-methylenediphenyl diisocyanate as obtained using different theoretical approaches.

We demonstrate that the molecule is chiral and that for each chirality, three different structures, differing in the orientations of the isocyanate groups, can be identified. The molecule is soft against certain geometry transformations and can, accordingly, easily take a structure that is optimal for the formation of covalent bonds with a substrate. Infrared spectroscopy may be used in identifying these covalent bonds, and therefore, these spectra were calculated, and we identify the most relevant vibrations in this context. Finally, changes in the properties when the monomer was modified or when it was allowed to interact with other molecules were studied, too.



INTRODUCTION

Adhesion is of fundamental importance for very many technological applications including, e.g., painting and glueing. In fact, glueing offers a very attractive approach for joining different metals without welding that involves heating the materials up locally to such high temperatures that the materials' properties may be affected negatively.¹ However, glueing of two metals will only then work if the glue is able to form strong chemical bonds with both metals. Accordingly, much effort is devoted to identifying and studying the interactions between the glue and the metal.²

In practice, a glue contains monomers that will bond covalently to the two materials that will be glued together. Subsequently, a polymerization process will connect the monomers at the two different materials and, thus, create a strong connection between the latter.³ The first important step is accordingly the formation of a covalent bond between a single monomer and a metal that even may be oxidized and that may also contain other adsorbants on the surface. Thereby, it is of advantage to use a monomer that is so flexible that it easily can adapt its structure to that of the surface. The complete system consisting of monomer(s) plus surface is too complex to allow for a direct identification of the covalent bonds between the metal and the monomer. Instead, indirect measurements are most often used in identifying those bonds, including, for

instance, vibrational spectroscopy. Thus, the formation of the covalent bond will change some of the vibrational properties of the monomer. Detecting such changes may accordingly imply the existence of a covalent bond, but by comparing with results of accurate theoretical studies, it becomes possible not only to identify the existence of a covalent bond but also to identify exactly which type of bond is formed and, thereby, in addition obtain information on the structure of the substrate. This approach has been used, e.g., by Schneider et al.⁴ for the study of adhesion of maleic anhydride on native aluminum oxide.

In the present work we will study the properties of the monomer 4,4'-methylenediphenyl diisocyanate (4,4'-MDI) that participates in a polymerization leading to the formation of polyurethane.⁵ Accordingly, 4,4'-MDI is an important system for glues. Its structure is shown in Figure 1.

Recently, Rodziewicz and Goclon studied 4,4'-MDI theoretically.⁶ Many of their findings are supported by our results but there are also several differences. Thus, as we will demonstrate, the system has more different structures than what was found in the study of Rodziewicz and Goclon. In addition, besides structure, their main goal was to identify various noncovalent

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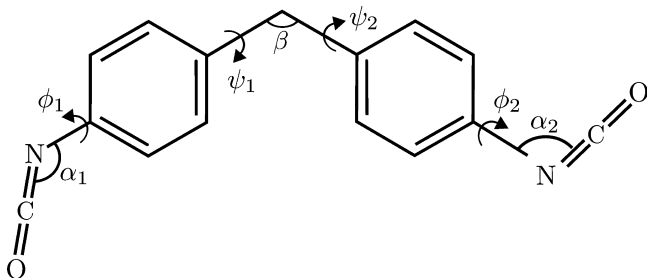


Figure 1. Schematic representation of 4,4'-methylenediphenyl diisocyanate (4,4'-MDI) including the geometrical parameters that we will focus on.

intramolecular interactions, whereas we focus on structural and vibrational properties of 4,4'-MDI.

To understand this molecule, we will already here discuss briefly the main findings of our work regarding its structure. Each of the two isocyanate groups, NCO , is lying in the plane of that phenylene ring, C_6H_4 , to which it is attached, which is in agreement with the findings of Rodziewicz and Goclon.⁶ We set the two rotational angles, ϕ_1 and ϕ_2 , equal to 0 or π in this case. On the contrary, the two bond angles α_1 and α_2 are not identical to π so that two different situations occur depending on whether an isocyanate group points “down” (as in the left part of Figure 1) or “up” (as in the right part of Figure 1). This gives us three different structures, i.e., both NCO groups in down orientation (hereafter labeled dd), both in up orientation (labeled uu), or one in up and one in down orientation (labeled ud or du). However, steric hindrance between two hydrogen atoms attached to carbon atoms of the different phenylene rings (Figure 1) prevents the two phenylene rings from lying in the same plane in which case the two rotational angles ψ_1 and ψ_2 would be set equal to 0 or π . Instead, it turns out that these two angles take essentially the same value whereby a chiral structure results whose chirality depends on the sign of the roughly common value of ψ_1 and ψ_2 . Here we will not distinguish between the two du and du structures (that actually are indistinguishable), neither between structures of different chirality.

In their *ab initio*, molecular-dynamics calculations, Rodziewicz and Goclon⁶ identified four structures that, however, do not cover all the different possibilities mentioned above. Thus, their structures **a** and **b** differ in chirality from their structures **c** and **d**. Moreover, whereas **a** corresponds to a dd structure, the other three are all of the ud or du type, although the authors report somewhat different total energies and dihedral angles for the latter. This last finding is most likely due to the very weak dependence of the total energy on certain structural parameters, as found in both their and our work to be discussed below.

In the present work we will demonstrate that the three different structures resulting from different orientations of the NCO groups have very similar energies and also that only small energy barriers separate those. Therefore, when 4,4'-MDI is adsorbed on some substrate, the NCO groups can arrange themselves to give an optimal interaction with the substrate. Thus, the presence of a covalent bond between 4,4'-MDI and some substrate will first of all affect the isocyanate groups and, therefore, we will focus on vibrations that are localized to those.

The purpose of the present work is to study those properties of 4,4'-MDI that are relevant for a theoretical description of results that can assist experimental studies of adsorption of the

molecule on some substrate. This means that we will discuss those structural parameters that can be varied relatively easily without large energy costs. Thus, we will study the dependence of the total energy on some of the angles that are shown in Figure 1. Moreover, we will study the relative energies of the three different structures mentioned above. For vibrational spectroscopy, properties related to the dipole moment are relevant, a quantity that it is difficult to calculate accurately. Therefore, we will also discuss the total dipole moment of the different structures. Also the frequencies and infrared intensities for those vibrations that involve mainly the NCO groups will be studied. In particular, we will study these properties as a function of computational approach, including size and type of a basis set as well as type of approximate density functionals.

Because the experimental studies on the 4,4'-MDI deposited on a substrate may not involve a single 4,4'-MDI molecule, we will also study how the properties change when the 4,4'-MDI molecule is interacting with some other molecule. This other molecule will be either a second 4,4'-MDI molecule or a single tetrahydrofuran (THF) molecule, $\text{C}_4\text{H}_8\text{O}$, that can be used in rinsing the samples when 4,4'-MDI is adsorbed on some metal surface.⁷ Also the consequences of modifying the 4,4'-MDI molecule on its structural and energetic properties will be studied whereby additional information on those properties of 4,4'-MDI is obtained.

This paper is organized as follows. In the next section we describe the methodology used in this paper, then we present our results and the paper is closed, summarizing and drawing the main conclusions.

METHODOLOGY

Considering a single 4,4'-MDI molecule, we first tested the performance of two density functionals, i.e., the B3LYP^{8–10} and the PBE^{11,12} functionals using 15 different basis sets: 6-31G, 6-31G+, 6-31G++, LANL2DZ, 6-311G, 6-311G+, 6-311G++, 6-31G(d), 6-31G+(d), 6-31G+(d,p), 6-31G++(d,p), 6-311G(d), 6-311G+(d), 6-311G+(d,p), and 6-311G++(d,p). The molecule was relaxed without constraints in each calculation and we ensured that it possessed no imaginary vibrational frequencies.

Subsequently, starting from the optimized dd structure, we mapped out all the possible combinations of (ψ_1, ψ_2) (in steps of 10°) and carried out a single-point total-energy calculation to identify stable isomers. From this analysis, it turns out that there are only three different isomers, i.e., the dd, ud, and uu structures. These three were further investigated using the BLYP method^{9,13} and the semiempirical PM6 method,¹⁴ together with the already mentioned PBE and B3LYP methods and different basis sets. Even though the PM6 method cannot be considered as an appropriate method for the (smaller) molecules of the present study, it could very well be so for larger systems consisting of more molecules and eventually also a surface, all interacting with each other. Therefore, we found it relevant to study the performance of this method, too. All calculations were carried out with Gaussian 09 program package.¹⁵

We will concentrate on the relative energy of the three structures and their total dipole moment. Also the geometrical parameters shown in Figure 1 are of our interest, whereby, for symmetry reasons, for the uu and dd structures, $\psi_1 = \psi_2$, $\phi_1 = \phi_2$, and $\alpha_1 = \alpha_2$ (see, however, below). In addition, we calculated the infrared (IR) vibrational spectra using the different approaches but will here report only some typical results. Finally, we studied the changes that would occur when

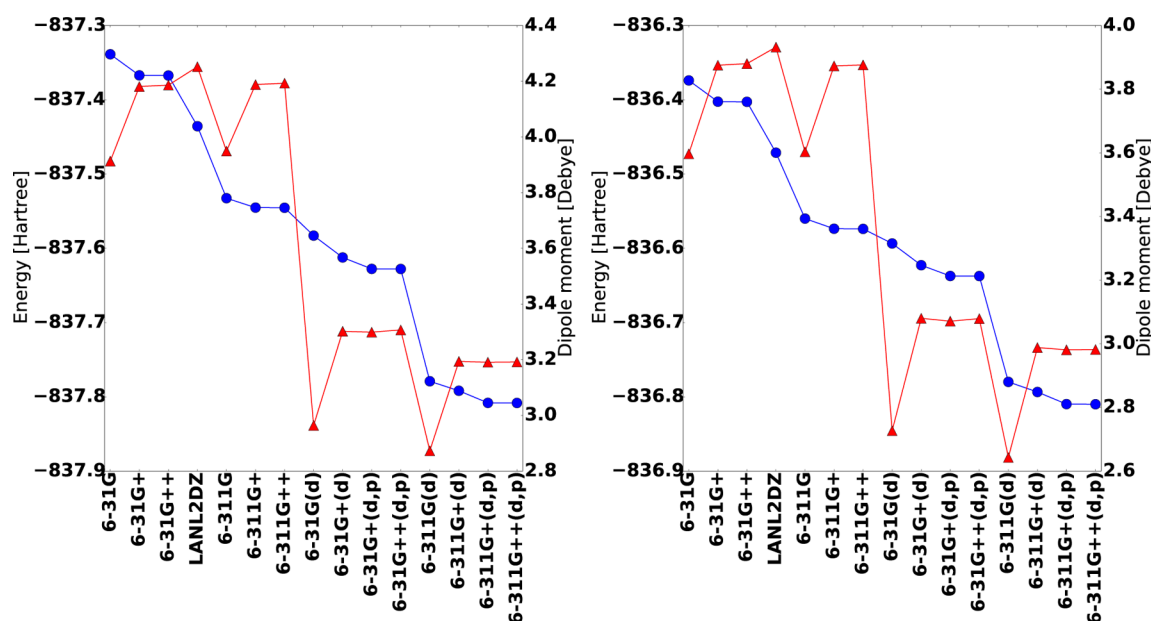


Figure 2. Total energy (circles) and the dipole moment (triangles) as a function of quality of the basis set from the B3LYP (left) and PBE (right) calculations for the dd structure.

Table 1. Calculated Properties for Different Computational Approaches^a

method	basis set	$\Delta E(\text{dd})$	$\Delta E(\text{ud})$	$\Delta E(\text{uu})$	$\mu(\text{dd})$	$\mu(\text{ud})$	$\mu(\text{uu})$
PM6		0	1.86	3.58	2.961	3.218	3.414
BLYP	6-31++G	0	0.62	2.46	3.967	3.667	3.288
	6-31+G(d)	0	1.74	4.09	3.187	2.979	2.584
B3LYP	6-31++G	0	0.73	1.96	4.191	3.907	3.552
	6-31+G(d)	0	1.39	3.74	3.305	3.012	2.653
PBE	6-31G	0	1.75	1.47	3.586	3.318	2.999
	6-31+G	0	1.71	1.45	3.866	3.560	3.196
	6-31++G	0	1.94	1.63	3.872	3.561	3.195
	6-31G(d)	0	1.07	2.85	2.719	2.493	2.218
	6-31+G(d)	0	1.69	3.41	3.072	2.827	2.464
	6-311+G(d)	0	1.21	3.98	2.983	2.698	2.355
	6-311++G(d,p)	0.52	0	2.78	2.980	2.692	2.373

^a $\Delta E(xy)$ gives the total energy in millielectronvolts of the xy structure relative to the most stable structure, whereas $\mu(xy)$ gives the dipole moment in Debye of the xy structure.

either modifying the 4,4'-MDI molecule or letting it interact with some other molecule.

RESULTS AND DISCUSSION

Energetic Properties of a Single 4,4'-MDI. At first, we show in Figure 2 the total-energy differences and the dipole moment for the dd structure from two types of calculations, i.e., B3LYP and PBE, as functions of the quality of the basis set. The basis sets are sorted in order of decreasing total energy. Naturally, the lowest energy is obtained with the largest basis set as the variational principle states. However, we can identify certain trends in the energy and dipole moment caused by different types of basis sets. For example, one can observe that the energy decrease is larger when d-polarization functions are included to a double- ζ basis set, i.e., 6-31G(d), than when the calculations are performed with a triple- ζ basis set (6-311G) and only smaller energy variations are obtained when including diffuse functions. Nevertheless, these latter are important for the charge distribution as we can see for the dipole moment where the lowest values, which are markedly different from the other ones, were obtained without diffuse functions. The large

drop in dipole moment is, again, due to the presence of polarization functions in the basis sets. On the contrary, including diffuse (++) and/or p-polarization functions to the H atoms does not change appreciably the total energy or the dipole moment.

Some key quantities are given in Table 1 for various computational approaches. It is interesting to notice that despite the stronger variations in the absolute values of the total energies, there is a general agreement that the relative total energies among the different structures all are small, i.e., just some few millielectronvolts, which is understandable because the structures differ only in the orientation of each isocyanate group lying in the plane of one phenylene group relative to the orientation of the plane of the other phenylene ring and isocyanate group. Only the PBE calculations with the largest basis set predict a different energetic ordering, although the very small total-energy differences make it probable that numerical noise is the reason for this.

On the contrary, because the dipole moment has a large contribution from the isocyanate groups, their orientations have significant impact on the value of the total dipole moment.

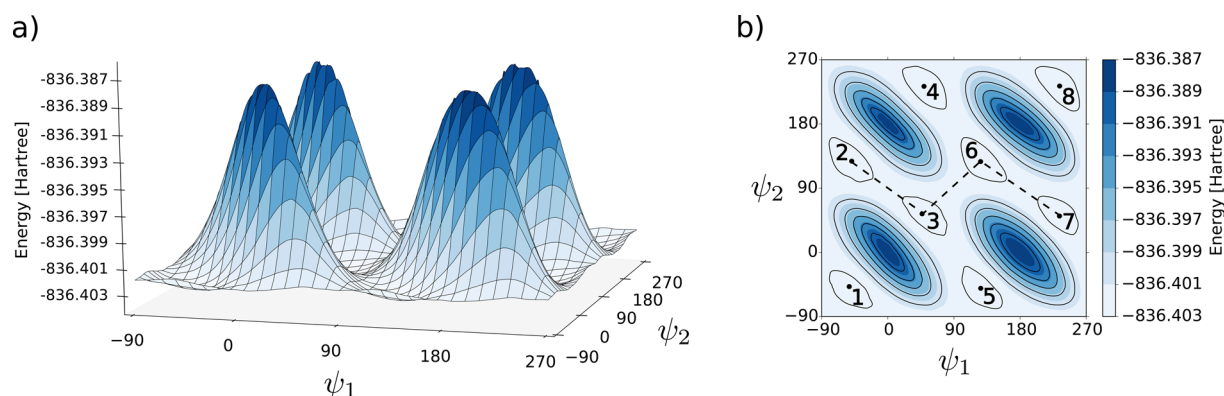


Figure 3. (a) 3D view and (b) contour plot of the total energy as a function of the two dihedral angles ψ_1 and ψ_2 , obtained through single-point calculations with the PBE functional and the 6-31+G(d) basis set. All other structural parameters were kept fixed at the values of the global minimum (3, the dd structure). Also a path connecting four fundamentally different structures is shown.

Here, the fact that the dipole moment of the ud structure is not simply the average of those of the dd and uu structures (although close to) indicates that there is some “cross-talking” between the two parts of the molecule. Moreover, the PM6 calculations predict a reverse ordering of the values of the dipole moments, which must be taken as a failure of this method. Finally, because the different structures have very comparable total energies, an experimental study of 4,4'-MDI will consider an essentially equal mixture of all three structures, which also will be the case for the dipole moment. For this, a value of 2.75 D has been reported.¹⁶ When compared with the results of Table 1, this experimental value is seen to be consistent with the PBE values for the three largest basis sets. Moreover, for the same basis sets, the PBE values are somewhat smaller than the B3LYP values, although the differences may not be so significant that a general conclusion can be made.

Next, we will discuss the dependence of our results on the ψ angles shown in Figure 1. Our results demonstrate that this is the softest geometrical deformation, also because the normal modes with the lowest frequencies correspond to vibrations where the ψ 's vary with the isocyanates moving so that they remain in the same plane as the phenylene rings ($\phi_1 \simeq \phi_2 \simeq 0$). For the normal modes with the fourth and fifth lowest frequencies, the isocyanates are moving out of the planes of the phenylene rings. We will discuss this case later. Using the PBE functional and the 6-31+G(d) basis set, we varied each of the two angles ψ_1 and ψ_2 in steps of 10° in the range from -90° to $+270^\circ$ and carried out a single-point total-energy calculation. The $(0^\circ, 0^\circ)$, $(0^\circ, 180^\circ)$, $(180^\circ, 0^\circ)$, and $(180^\circ, 180^\circ)$ structures correspond to 4,4'-MDI molecules where all the atoms are in the same plane (except for the two H atoms of the methylene group), as it is depicted in Figure 1. Thus, the resulting steric hindrance between two H atoms of different phenylenes leads to the steep increase in the total energy for these structures as shown in Figure 3.

The calculations resulted in eight local total-energy minima, marked in Figure 3, that turned out to be different, although in some cases the differences can only be identified when being able to distinguish among the atoms (as is the case in a calculation, but hardly in an experiment). Moreover, the total-energy surface possesses a very flat region separating the different minima. The fact that the total energy changes very little in this flat region means at first that it often is difficult to identify the local minima precisely and, second, that smaller differences in the computational approach like in the

approximate density functional and/or in the basis set easily lead to larger changes in the optimized values of the dihedral angles ψ_1 and ψ_2 . The finding that the molecule very easily can change structure is in full agreement with the ab initio molecular-dynamics results of Rodziewicz and Goclon.⁶

For all structures we found that $\psi_1 \simeq \psi_2 \neq 0$ (modulus 180°), whereby the two structures with $(\psi_1, \psi_2) \simeq (\psi_0, \psi_0)$ and $(\psi_1, \psi_2) \simeq (-\psi_0, -\psi_0)$ with ψ_0 lying in the interval between 0 and 90° differ only in chirality. Then, changing $\psi_i \rightarrow \psi_i \pm 180^\circ$ corresponds to changing an up position of the corresponding isocyanate group to a down position, or vice versa. In total, this gives the following four structures with the same chirality, where the numbers refer to those of Figure 3:

$$\begin{aligned}
 6: & \text{ dd } (\psi_1, \psi_2) \simeq (\psi_0, \psi_0) \\
 5: & \text{ du } (\psi_1, \psi_2) \simeq (\psi_0, \psi_0 + 180^\circ) \\
 2: & \text{ ud } (\psi_1, \psi_2) \simeq (\psi_0 + 180^\circ, \psi_0) \\
 1: & \text{ uu } (\psi_1, \psi_2) \simeq (\psi_0 + 180^\circ, \psi_0 + 180^\circ)
 \end{aligned} \quad (1)$$

whereas an equivalent set of structures but with the opposite chirality consists of

$$\begin{aligned}
 8: & \text{ dd } (\psi_1, \psi_2) \simeq (360^\circ - \psi_0, 360^\circ - \psi_0) \\
 7: & \text{ du } (\psi_1, \psi_2) \simeq (360^\circ - \psi_0, 180^\circ - \psi_0) \\
 4: & \text{ ud } (\psi_1, \psi_2) \simeq (180^\circ - \psi_0, 360^\circ - \psi_0) \\
 3: & \text{ uu } (\psi_1, \psi_2) \simeq (180^\circ - \psi_0, 180^\circ - \psi_0)
 \end{aligned} \quad (2)$$

However, as mentioned above, for our purposes the structures differing only in chirality are equivalent as is the case for the ud and du structures. Thus, the eight local total-energy minima can be separated into three structures with different properties.

Rodziewicz and Goclon⁶ performed PBE calculations on 4,4'-MDI using plane waves as basis functions. They report that a structure of the dd type has the lowest total energy, whereas that of structures of the du/ud type is 1.1 ± 0.2 meV higher, a finding that fits our results very well.

Two possible transformations among the uu, du, ud, and dd structures (irrespective of chirality of the resulting structures) can be obtained by varying one ψ angle or by varying one ϕ angle, with the corresponding isocyanate leaving the plane of the phenylene. We will at first study the first possibility. We carried out a more careful energy scan fixing one ψ angle in

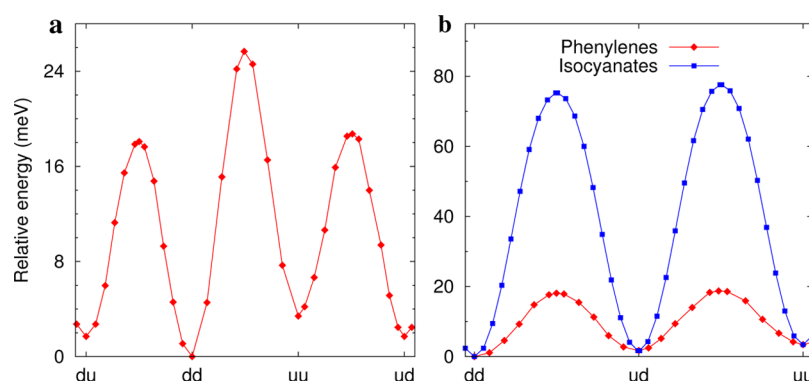


Figure 4. (a) Variation in the total energy along the path of Figure 3, i.e., fixing one ψ angle in steps of 10° and allowing all others parameters to relax. (b) Comparison between the transformation (a) with that made by rotating only one isocyanate group.

Table 2. Calculated Angles (cf. Figure 1) in Degrees for Different Computational Approaches^a

method	basis set	$\alpha(\text{dd})$	$\alpha(\text{ud})$	$\alpha(\text{uu})$	$\psi_1/\psi_2(\text{dd})$	$\psi_1/\psi_2(\text{ud})$	$\psi_1/\psi_2(\text{uu})$
PM6		136	136	136	58/58	57/58	58/58
BLYP	6-31++G	149	149	149	57/57	54/58	53/58
	6-31+G(d)	140	140	140	60/60	62/61	60/60
B3LYP	6-31++G	154	154	154	55/55	55/55	52/56
	6-31+G(d)	141	141	141	59/59	54/60	58/58
PBE	6-31G	149	148	149	55/55	54/52	52/52
	6-31+G	149	149	149	52/52	55/51	55/48
	6-31++G	149	149	149	52/52	51/54	48/54
	6-31G(d)	139	139	139	54/54	58/51	53/53
	6-31+G(d)	140	140	140	55/55	55/55	55/55
	6-311+G(d)	139	139	140	55/55	60/50	50/56
	6-311++G(d,p)	139	139	140	54/54	60/50	50/59

^aWe report only the parameters which exhibit more variation, i.e., $\alpha \simeq \alpha_1 \simeq \alpha_2$, as well as ψ_1 and ψ_2 for the three 4,4'-MDI structures: dd, ud, and uu.

steps of 10° and allowing all others parameters to relax. The parameters of the initial geometries were those of the closest total-energy minimum. We emphasize that along this path, chirality changes from the du structure to the dd structure, from the dd structure to the uu structure, and again from the uu structure to the ud structure. In fact, for the dd \leftrightarrow uu transition, we had to fix both ψ angles, because fixing only one leads to the dd \leftrightarrow ud transition, which is equivalent to the previous one. The resulting total-energy variations are shown in the left panel of Figure 4 and demonstrate clearly that the system is very soft against a concerted variation of the two dihedral angles ψ_1 and ψ_2 as long as structures with a large steric hindrance are avoided. Moreover, the very small total-energy differences among the dd, uu, and du structures are clearly seen, too. Thus, under normal conditions, the 4,4'-MDI molecule can take a structure that is dictated by surroundings like, e.g., surfaces or a solvent. Moreover, a mixture of different structures will most likely be found, too.

Another way of changing the structures among uu, dd, and ud/du is to rotate the isocyanate groups, i.e., to change the angles ϕ_1 or ϕ_2 . Thereby, the chirality of the structures will not change and, accordingly, it is not exactly the same path as that shown in Figure 3 for which the chirality is changed. However, as shown in the right panel of Figure 4, this transition involves larger total-energy changes although the energy barriers among the different structures still are fairly small (about 0.08 eV).

Finally, a simple model can explain at least qualitatively the small total-energy differences among the different structures. Thus, as we have argued, the major contribution to the total dipole moment comes from the isocyanate groups, although the

individual contributions from each isocyanate group may not be parallel to this group (because also parts of the phenylene rings will be polarized and therefore contribute to the dipole moment). Assuming that only these groups contribute to the total dipole moment, we can use the values for the dd and uu structures in estimating the size and orientations of these contributions. Subsequently, assuming that they have a separation of $R = 20$ au, the total-energy difference between the uu and dd structures is of the order of 0.5–1 meV, which is surprisingly close to the values reported in Table 1. Thus, these dipole–dipole interactions may very well be responsible for the small differences in the total energy. Furthermore, this estimate suggests also that dispersion interactions, originating from induced dipoles that most likely will be much weaker than the permanent ones and with a much faster decay as a function of R (R^{-6} instead of R^{-3}), will not play any role for the present systems.

Structural Properties of a Single 4,4'-MDI. Next, we will discuss the calculated structural properties of a single 4,4'-MDI molecule as found using different theoretical approaches. Above, we have argued that for the present purpose, i.e., to identify a computational approach for studying a 4,4'-MDI molecule adsorbed on some substrate, the angles shown in Figure 1 are the most important structural parameters. Therefore, in Table 2, we report those calculated values that vary mostly with different functionals and basis sets. The β angle, being the bond angle between the sp^3 orbital hybrids of the methylene, has a value that does not change strongly for different approaches, being always between 114° and 115° except for the semiempirical PM6 method for which it becomes

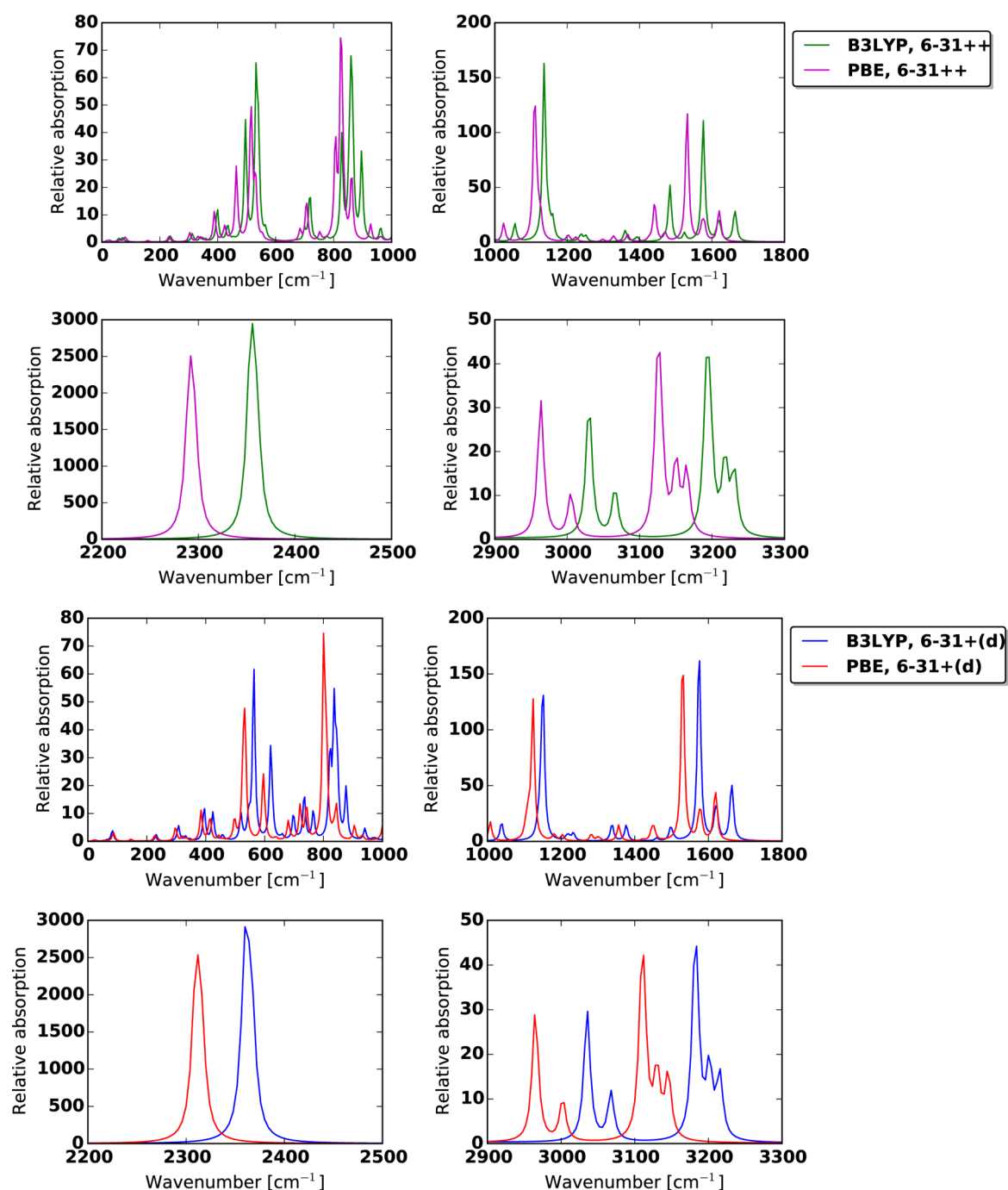


Figure 5. Theoretical IR spectra calculated with two different basis sets as well as the B3LYP and the PBE approaches for the dd structure. The peaks were broadened with Lorentzians with a fwhm of 10 cm^{-1} .

112° . On the contrary, in all optimizations we obtained $\phi_1 \simeq \phi_2 \simeq 0$. Therefore, these parameters are not included in Table 2.

The situation is a little more tricky for the values of $\alpha_1 \simeq \alpha_2 \simeq \alpha$. For those, the results depend strongly on the size of the basis set although a general trend can be observed; i.e., the calculations made with basis sets that include polarization functions give smaller values ($\alpha \simeq 140^\circ$), whereas those where the polarization functions are absent give larger values ($\alpha \simeq 150^\circ$). This may be compared with the results of the earlier study of Adamo and Barone.¹⁷ These authors used a large basis (equivalent to the largest one of the present study) and studied the performance of more approximate density functionals for a set of smaller molecular systems. Using this large basis set, they

found only smaller deviations in the optimized values for bond and dihedral angles, suggesting that this may be the case also for other related systems (and we consider the 4,4'-MDI molecule as being related to those of the study of Adamo and Barone). This is, however, only then the case if a sufficiently large basis set is used, which is possible for smaller molecular systems but only with large difficulties for larger systems like the 4,4'-MDI interacting with some substrate. Therefore, for systems like the latter, it is of crucial importance to identify a computational approach that simultaneously can be used for the large systems and that leads to accurate results. Our results suggest that this is the case with basis sets of the type 6-31G+(d) or better. Here, diffuse and polarization functions are

Table 3. Calculated IR Properties for Different Computational Approaches^a

method	basis set	$\nu(\text{dd})$	$\nu(\text{ud})$	$\nu(\text{uu})$	$I(\text{dd})$	$I(\text{ud})$	$I(\text{uu})$
PM6		2206/2214	2206/2214	2206/2214	66.4	46.6	9.5
BLYP	6-31++G	2245/2250	2246/2251	2246/2251	52.4	34.3	10.4
	6-31+G(d)	2268/2273	2268/2273	2268/2273	56.1	44.8	8.5
B3LYP	6-31++G	2354/2360	2354/2360	2354/2360	51.0	34.3	12.5
	6-31+G(d)	2359/2365	2359/2365	2359/2365	59.3	39.4	8.2
PBE	6-31G	2305/2309	2305/2310	2306/2310	56.4	34.7	9.9
	6-31+G	2289/2294	2290/2295	2290/2295	56.7	35.5	9.8
	6-31++G	2289/2294	2290/2295	2290/2295	57.1	35.3	9.6
	6-31G(d)	2326/2331	2326/2331	2327/2331	63.5	37.5	6.8
	6-31+G(d)	2308/2313	2308/2314	2309/2314	63.3	42.1	7.3
	6-311+G(d)	2309/2315	2309/2315	2310/2316	64.7	38.3	6.3
	6-311++G(d,p)	2309/2315	2309/2315	2310/2315	65.0	38.0	6.8

^a $\nu(xy)$ gives the frequencies of the two vibrations with the dominating contributions from the isocyanate groups in cm^{-1} of the xy structure. In each case, the slash separates the value for the lower frequency from that of the higher one. I is the ratio (in %) of the intensity of the second peak relative to that of the first peak.

required to obtain an accurate description of the dipole moment and related properties.

Regarding the dihedral angles ψ_1 and ψ_2 , one can observe that they are not exactly related through changes according to eqs 1 and 2. Moreover, the $\psi_1 = \psi_2$ symmetry is always kept only for the dd structure, whereas the deviations found for the ud and uu structures can be up to $\pm 5^\circ$ from their average. Unfortunately, the results of Table 2 do not allow for making general conclusions about when this deviation occurs. Additionally, we found that if the $\psi_1 = \psi_2$ symmetry is imposed in some of those uu structures where that symmetry is absent, an imaginary vibrational frequency shows up. This disturbing finding may have its roots in “cross-talking” between the two isocyanates although it may have also other reasons.

When the B3LYP results are compared with those of the pure density-functional calculations (BLYP and PBE) using the same basis sets, there seems to be a general trend that the B3LYP leads to slightly larger bond angles than the other methods, whereas the semiempirical PM6 method performs well.

Finally, when comparing our PBE results for the dihedral angles ψ_1 and ψ_2 with those of Rodziewicz and Goclon,⁶ we observe some smaller differences. Thus, for the dd structure they report a value of 50° . For the ud/du structures, their values correspond to 51 , 55 , and 63° . This scatter is a further indication of the softness of the molecule against variation in the two dihedral angles.

Vibrational Properties of a Single 4,4'-MDI. One goal will be to use spectroscopy to identify the bonding between the 4,4'-MDI and a substrate, whereby, for instance, IR spectroscopy can be applied. The IR frequencies are determined from the second-order derivatives of the total energy with respect to nuclear coordinates and are, as such, more difficult to calculate accurately as is the equilibrium structure. Moreover, for the mode at frequency ν_k , the IR intensity is

$$I(\nu_k) \propto |\nabla_{\vec{u}_k} \vec{\mu}|^2 \quad (3)$$

where $\nabla_{\vec{u}_k} \vec{\mu}$ is the gradient of the dipole moment vector with respect to the normal coordinates of the k th mode, \vec{u}_k . As we have seen, only a larger basis set is capable of producing accurate values for the dipole moment, suggesting that it becomes even more difficult to obtain accurate values for the derivatives entering eq 3.

For each of the uu and dd structures, the two halves of the molecule, separated by the methylene group, are (expected to be) completely equivalent and related to each other through a C_2 rotation. Accordingly, the vibrational modes can be split into symmetric and antisymmetric ones, each having the same contribution from the two halves. The splitting in the frequencies of each pair of such modes gives information on the “cross-talking” between the two halves of the molecule. For the du/ud structures, this symmetry element is absent, but still, the vibrational modes will, in most cases, contain contributions from both halves of the molecule, although these will no longer be of equal size. Moreover, most modes will still occur in pairs as for the more symmetric uu and dd structures.

At first, we show in Figure 5 the full vibrational spectrum for the dd structure as calculated using different basis sets and different functionals. In general, the frequencies obtained with the B3LYP functional are higher than those of the PBE calculations as often is found (see below). On the contrary, the frequencies show also a (smaller) dependence on the size of the basis set whereby the intensities depend stronger on this size (for a more direct comparison, see previous section). The latter is easily understood from eq 3 together with the observations in the previous subsection concerning the accuracy with which the dipole moment can be calculated.

In their study of the performance of very many theoretical approaches and with a large basis set on a set of smaller molecules, Adamo and Barone¹⁷ found that most approaches gave mean absolute deviations for the vibrational frequencies of $30\text{--}70 \text{ cm}^{-1}$. The deviations from this general finding are, in the present study, not of relevance. For the present study, the much more recent work of Gorski et al.¹⁸ may be of much more relevance. They studied the performance of several different computational approaches, differing in the size of the basis set and/or the density functional, in calculating the vibrational properties of a single, planar, organic molecule. Thereby, both the frequencies and the IR and Raman intensities were calculated and compared with experimental information.

For the B3LYP approach they found that scaling the calculated frequencies by between 0.97 and 0.985, depending on the size of the basis set, would give the best agreement between experiment and theory, whereas for PBE a scaling of about 1.01 was optimal. With those scalings, a very good agreement between theoretical and experimental frequencies is obtained. This implies that the B3LYP frequencies in general

are higher by some few percent than the PBE frequencies. Our results, cf. Figure 5 and Table 3, confirm that including some Hartree–Fock exchange interactions, as in B3LYP but not in BLYP or PBE, gives higher vibrational frequencies, which in turn suggests that the B3LYP approach is less accurate in this respect.

For the IR intensities, Gorski et al.¹⁸ obtained a significantly less good agreement between theory and experiment, whereby B3LYP performed better than PBE. However, the correlation coefficients between experimental and theoretical intensities were as low as between 0.7 and 0.95, being smaller/larger when we concentrate on the out-of-plane/in-plane vibrational modes.

However, we emphasize that, when aiming at applying vibrational spectroscopy to identify covalent interactions between 4,4'-MDI and some substrate, it is not possible to identify a priori a scaling factor that will lead to an optimal agreement between experiment and theory. Instead, one will have to compare directly the unscaled experimental and theoretical spectra. Therefore, it is important to have a maximum amount of information on the influence of other factors on the vibrational spectra, these being computational or experimental inaccuracies or the interactions between 4,4'-MDI and other molecules.

In Figure 5, the most dominating feature appears at roughly 2300 cm^{-1} and is actually related mainly to the vibrations of the isocyanate groups and is, of the reasons explained above, split into two features. Thereby, the higher peak is due to the modes where the two isocyanate groups vibrate in antiphase, and the other feature, at a slightly higher frequency, comes from the in-phase vibration of the two isocyanate groups. In all the cases, the second feature has a lower intensity than the first one, because the changes in the total dipole moment from the two isocyanate groups then rather cancel each other instead of supporting each other.

In Table 3 we have collected the frequencies and relative intensities of those two peaks as found with different computational approaches. At first, it is clear that the three structures uu, dd, and du/ud give very close frequencies, whereas the relative intensity depends strongly on the structure. That structure dd, for which the total dipole moment (lying essentially along the bisector of β) is more parallel to the directions of the isocyanate groups, has both the largest total dipole moment and the largest changes in this when the atoms of the isocyanate groups vibrate along their bonds. It is obviously clear that this intensity can be a fingerprint of the structure although the very small total-energy differences among the different structures suggest that an experiment will see a mixture of all structures.

The relative intensities of the two features are in all cases smaller than 100%, which is in agreement with the considerations above. It is less obvious how to identify a correlation between computational approach and calculated relative intensities. However, for the dd structure there seems to be a trend to obtain smaller intensity differences for those calculations that lead to smaller values of α (including polarization functions), i.e., when the isocyanate groups are pointing “most down”. Other trends are hardly identifiable.

Finally, the vibrational spectra contain several other features. Those at higher energies (around 3000 cm^{-1}) are all due to C–H vibrations, whereas those at energies below 1800 cm^{-1} are due to vibrations involving the phenylene and/or methylene groups.

Modifying 4,4'-MDI. In this subsection we will obtain further information on the properties of 4,4'-MDI by comparing with those of related molecules. We considered the structures shown in Figure 6. By replacing the isocyanate

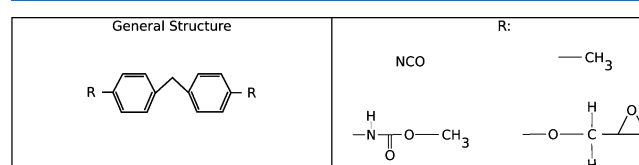


Figure 6. Schematic representation of the different molecules obtained by replacing the NCO groups of 4,4'-MDI by other groups. With reference to the right panel of the figure, these are (top, left) NCO (the reference system of 4,4'-MDI), (top, right) a methylene group, (bottom, left) a urethane-like group, and (bottom, right) a DGEBA-like group. For further details, see the text.

groups by methyl groups, we obtain a molecule with much less polarizing side groups and for which we may not obtain different “up” and “down” structures. On the contrary, the other substitutions in the figure lead to molecules that have functional groups resembling those of other monomers that are used in glues.

All these calculations were carried through using the PBE functional and the 6-31++G basis set but the study of the total-energy surface was not as complete as what we reported above for 4,4'-MDI. Therefore, the results of those calculations will be only briefly summarized.

At first, we consider the molecule obtained by replacing the isocyanate groups, NCO, by methyl groups, CH_3 . In this case, a distinction between up and down conformations turns out to be irrelevant. Again due to steric hindrance, the planes of the two phenylene rings are not parallel but have values for the ψ_0 angles of roughly $35\text{--}40^\circ$ so that also in this case chiral structures result. The methyl groups are essentially free to rotate about the C–C bonds whereby slightly different structures can result. In fact, they do differ in their values of the total dipole moment that, however, lying in the range 0.28–0.38 D, is considerably smaller than what was found for the 4,4'-MDI molecule. This confirms that a major part of the dipole moment of 4,4'-MDI has its origin in the isocyanate groups. Finally, estimating the barrier related to vary the dihedral angles ψ_1 and ψ_2 gave that this barrier is comparable with the values we have reported for 4,4'-MDI. This result was also found for the other systems to be discussed in the present subsection.

Second, we replaced the isocyanate groups by urethane-like groups, $-\text{NH}-\text{CO}-\text{O}-\text{CH}_3$, cf. Figure 6. In this case, we found indeed both up and down structures, i.e., uu, du, ud, and dd. Moreover, the end groups are polar and, as for 4,4'-MDI, the total dipole moment is large and depends strongly on the orientation of the two end groups. Thus, we obtained values of 2.59, 2.18, and 1.04 D. Furthermore, also for this molecule, the structures become chiral with values for ψ_0 around $35\text{--}42^\circ$, which is very similar to what we have found for the other molecules.

Next, we replaced the isocyanate groups by $-\text{O}-\text{CH}_2-\text{COCH}_2$, whereby the end groups resemble those of DGEBA (diglycidylether of bisphenol A) which is a very common diepoxy used in glues. Again, we found several different structures, differing in chirality and in up/down orientations of the end groups. The dipole moments became even larger, i.e.,

4.2, 2.5, and 2.1 D, whereas the values of ψ_0 were very similar to those obtained for the other molecules.

Finally, also replacing the methylene group CH_2 by $\text{C}(\text{CH}_3)_2$ introduces additional steric hindrance and, again, we have different structures depending on chirality and on up/down orientations of the end groups. Despite the additional steric hindrance, the optimized values of ψ_0 were very similar to those reported above, and also the dipole moment took very similar values.

Thus, the softness of the methylenediphenylene backbone is robust against several substitutions of relevance for monomers used in glues and there often are several different structures differing in “up” and “down” positions of the substitutions and/or in chirality. For most substitutions we found large total dipole moments of the monomers, a property that may be of relevance for the initial interactions between the monomers and the substrate to which the monomer will form a strong covalent bond.

4,4'-MDI Interacting with Other Molecules. Ultimately, 4,4'-MDI is supposed to form covalent bonds to an (oxidized) metal surface, which could suggest that it will also form strong covalent bonds to other molecules. Tetrahydrofuran (THF), $\text{C}_4\text{H}_8\text{O}$, can be used in rinsing the samples when 4,4'-MDI is adsorbed on some metal surface,⁷ and therefore, it is of relevance to study the 4,4'-MDI–THF interactions. Alternatively, it may also be possible that two 4,4'-MDI molecules will form some complex. To study these two systems, we used the PBE functional together with the 6-31++G basis set.

In both cases, we found several stable complexes that differ both in the internal structure of 4,4'-MDI (i.e., in chirality and in the “up” or “down” positions of the isocyanate groups) and in the relative position of the two interacting molecules. The total-energy differences between those were small, suggesting that they all may be found in experiment. Moreover, they possess all very similar vibrational properties. Therefore, we will here discuss only some few cases.

For 4,4'-MDI–THF an example of a stable complex is shown in Figure 7. In this case, the THF molecule was placed initially

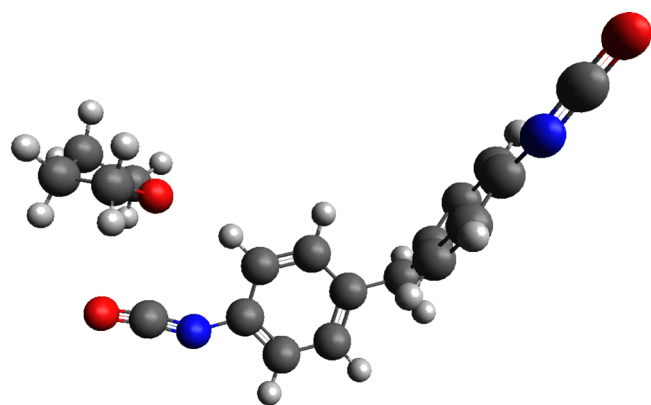


Figure 7. Optimized structure for the 4,4'-MDI–THF complex.

in the vicinity of one of the isocyanate groups and, subsequently, the complete structure was allowed to relax. The resulting structure suggests only a weak interaction between 4,4'-MDI and THF, as the distance between the oxygen atom of THF and carbon atom of the isocyanate group of 4,4'-MDI becomes roughly 3.2 Å, i.e., quite large. Thus, in this case we do not expect any competing interactions between 4,4'-MDI and THF when the concern is to create covalent

bonds to the metal surface. Also for the other stable complexes we found, the distances between atoms of different molecules were large and the intermolecular interaction energy was small.

Also two 4,4'-MDI molecules can form a loosely bonded complex. In Figure 8, we show several such conformations as

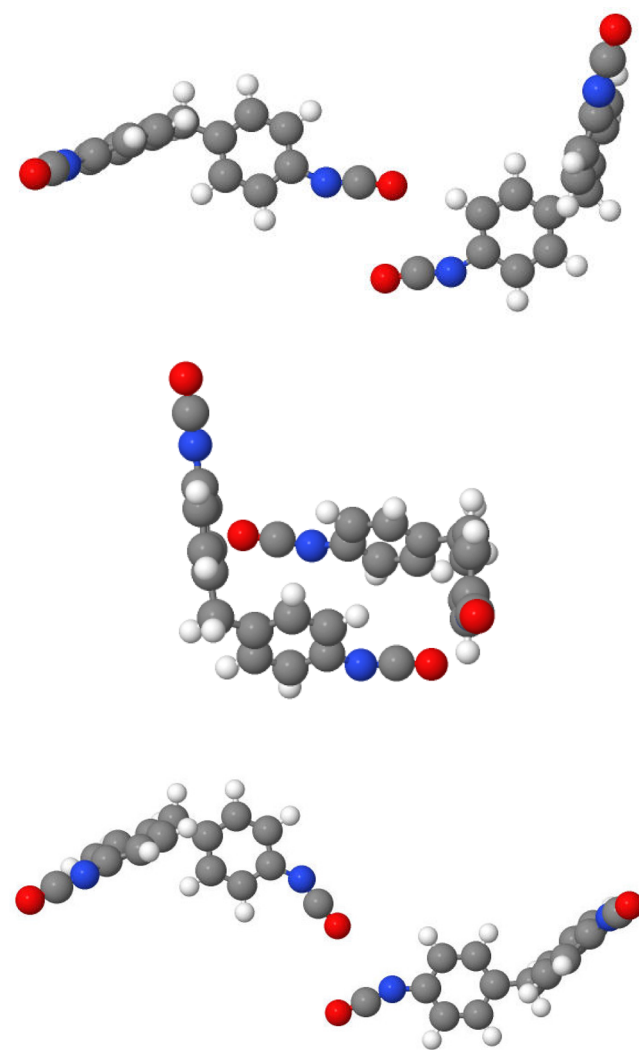


Figure 8. Different optimized structures for the 4,4'-MDI–4,4'-MDI complex.

obtained by relaxing locally various initial structures. In all cases, the closest distances between atoms of the two different molecules are above 3 Å, i.e., again longer than what is expected for covalent bonds.

In both cases, the energy difference between the two interacting molecules and the two isolated ones is very small: at most some few 0.1 eV. Even if these numbers do not include corrections for basis-set superposition errors or for dispersion interactions, the conclusion is clearly that the molecules do not form any strongly bonded complexes. However, in both cases an isocyanate group of one 4,4'-MDI molecule becomes relatively close to the atoms of the other molecule. Thus, when we focus on changes in the (e.g., vibrational) properties of the isocyanate groups when 4,4'-MDI forms a covalent bond to the metal surface, these changes may also be due to such interactions. Therefore, we show in Figure 9 the calculated IR spectra for a 4,4'-MDI–THF and for a 4,4'-MDI–4,4'-MDI

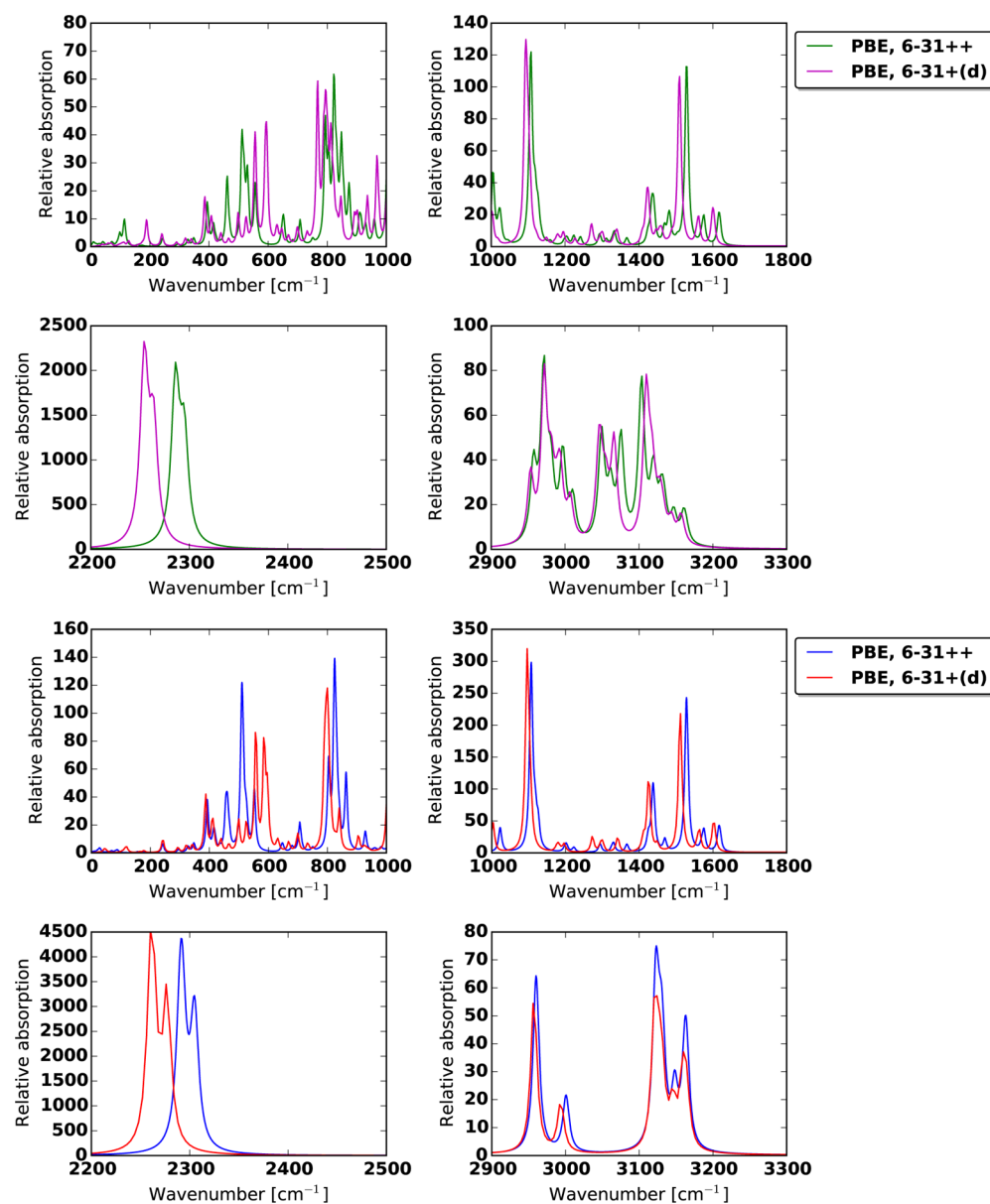


Figure 9. Theoretical IR spectra calculated with two different basis sets for the 4,4'-MDI molecule interacting with either (upper part) a THF molecule or (lower part) another 4,4'-MDI molecule. The peaks were broadened with Lorentzians with a fwhm of 10 cm^{-1} .

complex as calculated using the PBE functional and with two different basis sets. At first, we observe clearly the basis-set dependence of the absolute positions of the peaks that was mentioned in the previous results section.

For the two interacting 4,4'-MDI molecules, we have in total four vibrational modes that involve mainly the atoms of the isocyanate groups. Due to the interactions, these span now a larger frequency range, i.e., roughly 15 cm^{-1} , which is more than twice the splittings reported in Table 3 for a single 4,4'-MDI molecule. Even for the 4,4'-MDI molecule interacting with THF the two equivalent, vibrational modes experience a splitting that is increased compared with the case of the isolated 4,4'-MDI molecule, i.e., roughly 10 cm^{-1} . Thus, care has to be taken when we study this mode in an experiment devoted to identifying interactions between the 4,4'-MDI and a substrate: splittings of the two modes up to, e.g., roughly 20 cm^{-1} may have their roots in intermolecular interactions.

On the contrary, when comparing the complete vibrational spectrum of a single 4,4'-MDI with those of the 4,4'-MDI interacting with some other molecule, we see only very small changes in the other parts of the spectra. Whether this will change when 4,4'-MDI is interacting with a substrate will be a topic of a future work.

CONCLUSIONS

The overall goal of the present work was to study the properties of 4,4'-MDI, a molecule that is of relevance when two metals are glued together. Thereby we on the one side focused on those properties of 4,4'-MDI that make the molecule so flexible that it easily can adapt a structure that allows for the creation of strong, chemical bonds with the metal surfaces. Second, we aimed at identifying a computational approach that can be used in assisting experimental studies of 4,4'-MDI interacting with an (oxidized) metal surface. The latter system is so complex and large that a reasonable compromise between accuracy and

computational requirements has to be identified. In particular, it will be assured that those structural and vibrational properties are accurately described that are most important for the later applications. These properties are the values of the dihedral angles shown in Figure 1, the total energy variation related to changing the structure from one of the different ones to another, and the frequencies and IR intensities of those vibrations that involve the isocyanate groups. Moreover, we aimed at studying how those properties change when the 4,4'-MDI molecule is interacting with some other molecule or when it is slightly modified.

We found that 4,4'-MDI is chiral and that it, in addition, can take three different structures depending on the orientation of the isocyanate groups. The total-energy barriers separating those structures are very small (comparable to room temperature) and the total-energy differences even smaller, implying that 4,4'-MDI can change structure to an optimal one when it is adsorbed on a substrate. Different computational approaches all gave this, although some details differed.

The total dipole moment has its major origin in the charge distribution inside and close to the isocyanate groups, and therefore, their orientation influenced its value strongly. Here, a basis set including diffuse and polarization functions was required for obtaining an accurate description. IR spectra were calculated, too, because these can be used in experimentally studying the creation of covalent bonds between 4,4'-MDI and a substrate. As is often found, the frequencies from B3LYP calculations were in general higher than those of PBE calculations. The dominating feature was found to be due to vibrations of the atoms of the isocyanate groups and consisted of two unequally large peaks. Here, their relative height was found to depend strongly not only on the orientations of the isocyanate groups but also on the computational approach. It was hardly possible to identify trends in this case.

Finally, we found that related molecules obtained by replacing the isocyanate groups by other groups possessed very similar properties, whereby a substitution with methyl groups reduced the number of different structures and the total dipole moment significantly. We also found that 4,4'-MDI could form loosely bonded complexes that, however, affected the vibrational properties not substantially.

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Notes

The authors declare no competing financial interest.

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