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The excitation energies of 1,1′-bicyclohexylidene and 1,1′:4′,1″-tercyclohexylidene.
A comparison of multi-reference configuration interaction and perturbation theory approaches

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Abstract

The lowest valence transition energies of the first two homologues of the oligo(cyclohexylidene) series, viz. 1,1′-bicyclohexylidene (**1**) and 1,1′:4′,1″-tercyclohexylidene (**2**), were computed using multi-reference perturbation theory at the second (MR-MP2) and third order (MR-MP3). The results were compared to the previously reported results using a non-selected multi-reference single-double CI (Direct-CI) and a selected multi-reference single-double CI (MRDCI) approach, in order to obtain insight in the applicability of the MRDCI approach for the prediction of absorption spectra of large organic molecules. Calculations of the lowest valence excited states of 1,1′-bicyclohexylidene (**1**) showed that MR-MP3 gives energies comparable to those of Direct-CI; for the transition energies, MR-MP2 and MR-MP3 performed equally well. The calculations on the excited states of 1,1′:4′,1″-tercyclohexylidene (**2**) revealed that the MR-MP2 methodology is not reliable for the prediction of its transition energies, if the multi-reference character of the excited states increases. Although remarkable differences in the absolute transition energies were found, the assignments of the lowest valence transitions of 1,1′-bicyclohexylidene (**1**) and 1,1′:4′,1″-tercyclohexylidene (**2**) were similar at all levels of theory. © 1999 Elsevier Science B.V. All rights reserved.

1. Introduction

The UV absorption spectrum of the simplest representative in the oligo(cyclohexylidene) series, viz. 1,1′-bicyclohexylidene (**1**, Scheme 1) was studied in

detail [1–4]. In contrast to its analogue tetramethylethene, which possesses only one band at 7.0 eV that corresponds to the $\pi \rightarrow \pi^*$ transition [5] for **1** in the vapor phase (electron energy loss spectroscopy) as well as in solution (*n*-pentane), two bands were observed at 5.95 eV and 6.82 eV [1], and at 6.01 eV and 6.85 eV [2], respectively. In the solid-state polarized UV spectrum of a single crystal, the two bands were also discernible at 5.95 eV and 6.32 eV [3]. This suggests that both bands of **1** were

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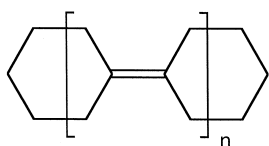
n=1: 1,1'-bicyclohexylidene (**1**)
n=2: 1,1':4',1"-tercyclohexylidene (**2**)

Scheme 1. n = 1: 1,1'-bicyclohexylidene (**1**) and n = 2: 1,1':4',1"-tercyclohexylidene (**2**).

valence transitions, since the intensity of Rydberg states would be diminished in solid-state and solution UV spectra. Similar results were obtained for a solid solution of **1** in stretched polyethylene films [4]. Although the band at 5.95 eV was assigned to a $\pi \rightarrow \pi^*$ transition, the assignment of the second band was less straightforward. It is suggested that it corresponds to a $\pi(CH_2) \rightarrow \pi^*$ excitation [1].

To obtain an unambiguous assignment for the valence transitions of **1**, configuration selected multi-reference single-double CI (MRDCI) [6–9] calculations were performed [10,11]. To exclude undesired mixing in of Rydberg states, the 6-31G basis set was chosen.

The first excited state had to be assigned to a $\pi \rightarrow \pi^*$ excitation (calc.: 9.47 eV), while the second transition corresponded to a $\pi \rightarrow \sigma^*$ transition (calc.: 10.65 eV). In line with experimental information [3,4], both transitions were calculated to be polarized parallel to the carbon–carbon double bond. The inclusion of polarization functions, using a 6-31G* basis set, did not alter the results. Hence, the 6-31G basis set gave a qualitative correct description of the lowest lying valence excited states of **1** [11].

However, the MRDCI program version currently in GAMESS-UK possesses three drawbacks, especially upon extension of this methodology for the calculation of the excited state energies and properties of larger molecules. Firstly, the number of electrons that can be correlated is restricted to thirty, which can cause a serious error in the transition energies. Secondly, only limited CI expansions are possible for larger molecules in a reasonable amount of time and disk space, severely restricting the amount of correlation allowed for. Lastly, all truncated CI approaches are not size-consistent. This can influence the transition energies of the excited states

of large molecules and this error will increase concomitant with the increasing size of the system.

To test the influence of the configuration selection procedure and the effect of neglect of electron correlation on the valence transition energies of **1**, nonselected multi-reference single–double CI (Direct-CI) [12] calculations were performed [10]. It was shown that, upon correlating all valence electrons and with the inclusion of all generated single and double excitations in the CI expansion, the transition energies were decreased from 9.47 to 8.29 eV for the $1A_g \rightarrow 1B_u$ transition and from 10.65 to 9.55 eV for the $1A_g \rightarrow 2B_u$ transition, respectively. At both levels of theory, the CI vectors were similar, indicating that a qualitative assignment of the lowest valence transitions can be made using the above-mentioned MRDCI approach.

To set up a framework for future calculations in which the excited states of large organic molecules, viz. in particular functionalized higher homologues of **1**, will be the subject of study, a comparison of the applicability of several methods is necessary. For large systems Direct-CI calculations are not feasible, and alternatives such as the MRDCI or MR-MP approaches may be used. In this study, we compared the MR-MP2 and MR-MP3 methods with previously reported MRDCI and Direct-CI results, as well as available experimental data. The objective was to gain insight into which method gives results that are accurate enough to explain the experimental results and are still computationally feasible for our intended future work, taking into account the recent developments of direct MRDCI methods [13–15]. We therefore chose to verify our previously reported MRDCI results for 1,1'-bicyclohexylidene (**1**) and 1,1':4',1"-tercyclohexylidene (**2**) [10] with MR-MP calculations.

It should be emphasized that Direct-CI calculations on the next higher homologue of **1**, viz. 1,1':4',1"-tercyclohexylidene (**2**), cannot be done in a reasonable amount of CPU time. The MRDCI calculations on **2** can be validated using the multi-reference MP2 (MR-MP2) and multi-reference MP3 (MR-MP3) methods [16–18]. A special variant of the MR-MP2 method is the frequently used CASPT2 approach [19–21]. The advantage of the MR-MP methodology is that it is size-consistent [22,23]. Moreover, the MR-MP method allows us to choose

the same reference configurations as in the MRDCI and Direct-CI calculations for a consistent comparison of the results.

In this paper, we first give a short description of the methods used, and then the results of the calculations on the excited state energies of **1** and **2** are presented.

2. Theory

In the MRDCI calculations, all single and double excitations are generated from a set of reference functions. For every configuration, the effect on the total energy is predicted and if it is larger than a preset threshold, the configuration is included in the CI expansion [6–9]. In the Direct-CI procedure, no configuration selection takes place, so all generated single and double excitations are included in the CI expansion [12].

Our multi-reference (MR) MP2/MP3 program is based on the early work of Wolinsky and Pulay [17,18] and implemented in our Direct-CI program [12]. It employs all single and double excitations generated from an internally contracted reference wave function. Since it does not employ the density matrix techniques developed by Roos and co-workers [20,21], it may be less efficient for a CASSCF reference function in CASPT2. It does, however, allow arbitrarily chosen reference wave functions and enables MR-MP3 calculations in a straightforward fashion.

The Hamiltonian is partitioned in the usual way into:

$$H = H_0 + V. \tag{1}$$

The Fock operator employed to construct the zeroth-order Hamiltonian H_0 is:

$$\hat{F} = \sum_{rs} f_{rs} \hat{E}_{rs}, \tag{2}$$

with

$$f_{rs} = h_{rs} + \sum_{ij} \langle \Psi_0 | \hat{E}_{ij} | \Psi_0 \rangle \left[(rs|ij) - \frac{1}{2}(ri|js) \right], \tag{3}$$

where $\hat{E}_{xy}$ are the unitary group generators. The zeroth-order Hamiltonian is defined as:

$$H_0 = P_0 \hat{F} P_0 + \sum_{i,j=0}^{1} P_{(i,j)S} \hat{F} P_{(i,j)S}$$

$$+ \sum_{i,j=0}^{2} P_{(i,j)D} \hat{F} P_{(i,j)D}, \tag{4}$$

where P_0 is the projection operator onto the ground state, $P_{(i,j)S}$ is the projector onto the singly excited states with i electrons excited out of the doubly occupied orbitals and j electrons excited into the virtual orbitals, and $P_{(i,j)D}$ is similar to $P_{(i,j)S}$ but projects onto the doubly excited states. This choice for the zeroth-order Hamiltonian ensures the size extensivity of our results [22,23].

The MR-MP CI vectors are back transformed to the configuration state basis and renormalized to unity. This ensures that the characterization of the states calculated using the MR-MP approach is consistent with the CI calculations.

3. Computational details

For all calculations, the 6-31G basis set was used. All CI and MR-MP calculations were performed at the RHF/6-31G geometry [10] and molecular orbitals (MOs). The MRDCI calculations were performed with the GAMESS-UK [24] package, using the MRDCI approach of Buenker and Peyerimhoff [8] and Buenker [9]. The highest 10 occupied MOs and lowest 88 virtual MOs were correlated in the MRDCI calculations, further denoted as 'MRD space'. The Direct-CI calculations were performed with the ATMOL [25] program package. In these calculations, only the 1s orbitals of the carbon atoms were frozen, resulting in 34 occupied and 102 virtual MOs. The MR-MP calculations were performed with the ATMOL [25] program package. Two sets of calculations were performed. A first set of calculations was performed in which the same orbitals were correlated as in the MRDCI calculations (MRD space), and an additional set of MR-MP calculations was performed in which the same orbitals were correlated as in the Direct-CI calculations.

Table 1
The chosen reference functions in the MR-MP calculations

State sym.	1,1'-bicyclohexylidene (**1**)	c^2	1,1':4',1''-tercyclohexylidene (**2**)	c^2
A_g	HF	0.93	HF	0.93
	(d) HOMO (b_u) $\rightarrow$ LUMO (a_g)	0.01	–	
B_u	(s) HOMO (b_u) $\rightarrow$ LUMO (a_g)	0.95	(s) HOMO (a_g) $\rightarrow$ LUMO (b_u)	0.83
			(s) HOMO-1 (b_u) $\rightarrow$ LUMO + 1 (a_g)	0.09
A_u			(s) HOMO (a_g) $\rightarrow$ LUMO + 6 (a_u)	0.10
			(s) HOMO-1 (b_u) $\rightarrow$ LUMO + 8 (b_g)	0.63

Only the configurations with $c^2 \geq 0.01$ in the MRDCI wavefunction of the lowest state of each symmetry are listed. For the A_u state of **2**, the contributions of the reference functions for the $4A_u$ state are listed. Single excitations from the Hartree-Fock (HF) determinant are denoted by (s) and double excitations by (d).

Both the Direct-CI and the MRDCI results were corrected for size-consistency errors by the Davidson method [26,27]. Note that the MRDCI results were not obtained by energy extrapolation [28]. In the Direct-CI and MR-MP calculations, the same reference configuration state functions were chosen. The reference set consisted of singly and doubly excited configurations in the space of the five highest occupied and nine lowest unoccupied MOs. The most important reference configurations are shown in Table 1.

Whereas in the MRDCI calculations on **1**, 56 740 configuration state functions (CSFs) of A_g and 69 783 CSFs of B_u symmetry were selected, in the Direct-CI calculations, 6 015 806 CSFs of A_g and 18 135 443 CSFs of B_u symmetry were considered. These numbers of CSFs resulted in 1 741 540 of A_g and 1 930 392 contracted states of B_u symmetry, which were treated in the MR-MP calculations.

In the MRDCI calculations on **2**, ca. 55 000 CSFs were selected, and in the MR-MP calculations

8 349 394 contracted states of A_g symmetry, 7 766 858 contracted states of B_u symmetry and 8 434 604 contracted states of A_u symmetry were considered. In Direct-CI calculations, using the same reference configurations, 108 001 918 CSFs of A_g, 67 949 272 CSFs of B_u and 69 107 646 CSFs of A_u symmetry had to be included in the CI expansion, indicating that these calculations are currently computationally not attractive.

To indicate the duration of these kind of calculations, typical timings for the largest calculations on **1** and **2** are summarized in Table 2.

4. Results

4.1. The valence excited state energies of 1,1'-bicyclohexylidene (1)

In our previous MRDCI study [10], it was shown that only the $1B_u$ and $2B_u$ excited states are of

Table 2
Timings (in hours) for the largest calculations on 1,1'-bicyclohexylidene (**1**) and 1,1':4',1''-tercyclohexylidene (**2**) performed on the CRAY C90 supercomputer

Method	1,1'-bicyclohexylidene (**1**) $1B_u$ state	1,1':4',1''-tercyclohexylidene (**2**) $1A_g$ state
MRDCI	0.6	0.7
Direct-CI	7.8	$-$ [a]
MR-MP2	0.5	2.6
MR-MP3	2.2	12.8

[a] Not currently feasible.

interest, since they correspond to the experimentally observed transitions. The excitation energies which were obtained using the MRDCI, Direct-CI, MR-MP2 and MR-MP3 methodologies are summarized in Table 3.

A comparison of the transition energies calculated at the MRDCI and those at the MR-MP3 level of theory using the MRD space reveals that for the $1B_u$ state, the transition energy decreases by ca. 0.8 eV upon going to the MR-MP3 level of theory, while for the $2B_u$ state, the transition energy decreases by only ca. 0.4 eV (Table 3). Since the same number of electrons is correlated, this difference is mainly due to the fact that the MR-MP3 methodology employs no configuration selection. Upon correlating all valence electrons, the MR-MP3 excitation energy towards the $1B_u$ state further decreased by ca. 0.6 eV, whereas for the $2B_u$ state the excitation energy decreased by ca. 1.1 eV. In going from the MRDCI to the MR-MP calculations, the transition energies for both excitations decreased by ca. 1.5 eV (Table 3). These results indicate that for a proper description of the $2B_u$ state, the lower lying MOs should be correlated. The configuration selection procedure produced only a small error. However, for the $1B_u$ state, electron correlation of the lower lying MOs was less important. This leads to the conclusion that for a proper description of the valence transitions, in which σ MOs are involved, the restricted number of electrons correlated can cause a large error in the transition energies.

The excitation energies, uncorrected for size-consistency errors, calculated at the Direct-CI level of theory are ca. 0.7 eV higher than the size-consistent MR-MP3 values. By applying the Davidson correction, the Direct-CI results are still approximately 0.4 eV higher than the excitation energies calculated at the MR-MP3 level of theory (Table 3). However, an inspection of the size-consistency corrected as well as the uncorrected Direct-CI results reveals that the size-consistency errors are practically constant, and small (0.3 eV) compared to the deviation of the calculated transition energies with the experimental values.

Whereas the transition energies calculated at the MR-MP2 level of theory are considerably lower than those at the other levels of theory, the excitation energies obtained at the MR-MP3 level are close to the Direct-CI results. This is in agreement with Werner's study, which shows that the MR-MP3 methodology is effective in approximating the Direct-CI results [29].

The assignment of the excitations is not influenced by the shifts in transition energies. The $1B_u$ state corresponds to the HOMO → LUMO excitation ($\pi \to \pi^*$) according to the CI vectors at all levels of theory in which this configuration has the largest contribution in the CI vector ($c^2_{\text{MRDCI}} = 0.92$; $c^2_{\text{MR-SDCI}} = 0.78$; $c^2_{\text{MR-MP}} = 0.66$). The CI vector of the $2B_u$ state is at all three levels of theory dominated by the HOMO → LUMO + 1 ($\pi \to \sigma^*$) excitation ($c^2_{\text{MRDCI}} = 0.87$; $c^2_{\text{MR-SDCI}} = 0.77$; $c^2_{\text{MR-MP}} = 0.64$).

The total energy of the ground state decreases more than the total energies of both excited states upon going from the MR-MP2 to the MR-MP3 level of theory, leading to a concomitant increase of the excitation energies (Table 3). Nonetheless, the difference between the first and second B_u excited states (exp. 0.87 eV) is in the same range for all methods, viz. 1.18 (MRDCI), 1.26 (Direct-CI), 1.05 (MR-MP2) and 1.09 eV (MR-MP3). This indicates that, al-

Table 3

The excitation energies towards the $1B_u$ and $2B_u$ states (in eV) of 1,1′-bicyclohexylidene (**1**)[a]

State symmetry	MRDCI	Oscillator strength (f)[b]	Direct-CI[c]	MR-MP2[d]	MR-MP3[d]	Exp. [1]
$1B_u$ (MRD Space)[d]	9.47	0.9401	8.29 {8.56}	7.14 (8.53)	8.01 (8.65)	5.95
$2B_u$ (MRD Space)[d]	10.65	0.1459	9.55 {9.89}	8.19 (10.58)	9.10 (10.21)	6.82

[a] Ground state total energies: MRDCI: -466.01168043 a.u.; Direct-CI: -466.94920140 a.u.; MR-MP2: -466.96005147 a.u.; MR-MP3: -467.04625575 a.u.

[b] Oscillator strengths (f) were calculated using the MRDCI wavefunctions.

[c] Size-consistency uncorrected Direct-CI results are between braces.

[d] The excitation energies calculated using the MRD Space are between parentheses.

though the absolute transition energies differ, the lowest valence excited states of **1** are described in an equivalent manner relative to each other at all levels of theory using the 6-31G basis set.

4.2. The valence excited state energies of 1,1′:4′,1″-tercyclohexylidene (2)

According to symmetry, only the B_u and A_u excited states of **2** have a non-zero oscillator strength. In the earlier MRDCI study [10], it was concluded that the lowest valence transitions of **2** are of B_u symmetry. Therefore, these states were studied using the MR-MP methodology (Table 4).

The transition energies for the $1B_u$ and $2B_u$ excited states decrease by ca. 0.7 eV in going from the MRDCI level to the MR-MP3 level of theory using the MRD space (Table 4). The excitation energy of the $1A_g \rightarrow 3B_u$ transition is nearly equal at both levels of theory. These results, together with the results obtained for **1**, confirm that for the description of the valence excitations in which σ MOs are involved, the low lying σ MOs should be correlated.

The $1B_u$ and $2B_u$ states were both assigned at the MRDCI level of theory [10] to $\pi \rightarrow \pi^*$ transitions, viz. the HOMO $\rightarrow$ LUMO and the HOMO-1 $\rightarrow$ LUMO + 1 transitions, respectively. The $3B_u$ state was assigned to a $\pi \rightarrow \sigma^*$ transition (HOMO $\rightarrow$ LUMO + 2) and the $4B_u$ state to a HOMO $\rightarrow$ LUMO + 9 excitation. At the MR-MP level of theory, the assignments of the two lowest ($1B_u$; HOMO $\rightarrow$ LUMO [$c^2_{MRDCI} = 0.83$; $c^2_{MR-MP} = 0.45$] and $2B_u$; HOMO-1 $\rightarrow$ LUMO + 1 [$c^2_{MRDCI} = 0.75$; $c^2_{MR-MP} = 0.37$]) transitions are similar. However, the higher

excited B_u states have more multi-reference character at the MR-MP level of theory. In the MRDCI calculations for the $3B_u$ state, c^2 for the HOMO $\rightarrow$ LUMO + 2 excitation equals 0.66, while at the MR-MP level the c^2 for this configuration is only 0.28. In the CI vector of the $4B_u$ excited state, the main configuration is the HOMO $\rightarrow$ LUMO + 9 excitation with $c^2_{MRDCI} = 0.82$ and $c^2_{MR-MP} = 0.31$. The increase of multi-reference character, i.e., the decrease of c^2 in the excited state CI vectors at the MR-MP level, is a consequence of the increase in the number of states considered in the MR-MP calculations. Since the CI vectors at the MRDCI and MR-MP level are similar, the trend in the oscillator strengths calculated at the MRDCI level has to be correct. Therefore, since the transition to the $4A_u$ excited state is the only one of the A_u states which has a non-zero oscillator strength, this transition energy was also recalculated using the MR-MP methodologies. The assignment (HOMO-1 $\rightarrow$ LUMO + 8 $c^2_{MRDCI} = 0.63$ and $c^2_{MR-MP} = 0.38$) of the $4A_u$ state is at the MR-MP level in line with the previous assignment at the MRDCI level of the theory [10].

The UV spectrum of **2** in solution (solvent *n*-pentane) consists of two broad absorption bands, centered at 6.02 and 6.78 eV [30]. The calculated transition energies at the MR-MP level are 6.77 eV (MR-MP2) and 7.83 eV (MR-MP3), for the $1B_u$ state and 7.05 eV (MR-MP2) and 8.52 eV (MR-MP3) for the $2B_u$ state, respectively. These transition energies are considerably lower than the MRDCI (9.23 eV and 10.08 eV) results (Table 4). The MR-MP2 excitation energies for the first and second excited states are close to the experimental values. However, at the

Table 4
The excitation energies for the B_u and $4A_u$ states (in eV) of 1,1′:4′,1″-tercyclohexylidene (**2**)[a]

Excited state symmetry	MRDCI	Oscillator strength (f)[b]	MR-MP2[c]	MR-MP3[c]	Exp.[d] [30]
$1B_u$ (MRD Space)[c]	9.23	1.8993	6.77 (8.44)	7.83 (8.60)	6.02
$2B_u$ (MRD Space)[c]	10.08	0.1956	7.05 (9.22)	8.52 (9.39)	6.78
$3B_u$ (MRD Space)[c]	10.87	0.1340	8.74 (10.65)	9.69 (10.67)	
$4B_u$ (MRD Space)[c]	11.56	0.1895	9.00 (10.81)	9.77 (10.70)	
$4A_u$ (MRD Space)[c]	12.18	0.1832	9.73 (11.86)	10.42 (11.42)	

[a] Ground state total energies: MRDCI: -697.73959400 a.u.; MR-MP2: -699.26482217 a.u.; MR-MP3: -699.38604538 a.u.

[b] Oscillator strengths (f) were calculated using the MRDCI wavefunctions.

[c] The excitation energies calculated using the MRD Space are between parentheses.

[d] Solution UV spectral data (solvent: *n*-pentane).

MR-MP3 level of theory, all excitation energies are again higher in energy than the corresponding MR-MP2 values.

The MR-MP2 ground state energy decreases by 0.12 a.u. upon going to the MR-MP3 level of theory (Table 4), while the total energies of the $1B_u$ and $2B_u$ states decrease by 0.08 and 0.07 a.u., respectively. This leads to an increase of the transition energies to the lowest excited B_u states. The trends found for **1**, viz. the MR-MP2 excitation energies, are lower than the MR-MP3 excitation energies, and consequently, closer to the experimental values (Table 3), are also observed for **2**.

The energy difference between the first and second transition is experimentally 0.76 eV. The total state energy difference between the $1B_u$ and $2B_u$ excited states at the MRDCI (0.85 eV) and MR-MP3 (0.69 eV) levels are in line with the experimental value. However, the difference in state energy of the $1B_u$ and $2B_u$ excited states at the MR-MP2 level of theory is much lower (0.28 eV) than the experimental value of 0.76 eV. In contrast to **1**, where all methodologies gave comparable results, a considerable difference is found in the case of **2** using the MR-MP2 approach. The observation that the relative positioning of the excited state energies is qualitatively wrong at the MR-MP2 level of theory for **2** can be rationalized by the fact that the excited states of **2** possess more multi-reference character than the excited states of **1**, and consequently H_0 is worse and the perturbation is larger for **2**. In general, perturbation theory at the second order then overestimates the correlation energy, resulting in transition energies, which are too low. Perturbation theory at the third order compensates for this effect, so the transition energies are increased upon going to third order perturbation theory [31].

We have shown that for large molecules, where concomitantly the multi-reference character of the excited states is increased, MR-MP2 theory gave a qualitatively wrong description of the excited state energies. Despite the deviation of the absolute transition energies with the experimental ones, the relative energy of the second excitation energy with respect to the first excited state, calculated using the MRDCI and MR-MP3 methods are in accordance with available experimental results. Moreover, as the calculated direction of polarization of the first two lowest

valence transitions of **1** are in line with the experimental data, the assignment of these two absorptions is correct. Therefore, the MRDCI and MR-MP3 methods correctly describe the lowest valence transitions of the oligo(cyclohexylidenes) **1** and **2**, using the 6-31G basis set.

5. Conclusions

The lowest valence excited states of 1,1′-bi-cyclohexylidene (**1**) and 1,1′:4′,1″-tercyclohexylidene (**2**) were calculated at the MR-MP2 and MR-MP3 level of theory. The results of these calculations for **1** and **2** were compared to earlier MRDCI and in the case of **1** also to Direct-CI calculations. For **1**, all methods predicted the UV absorption spectrum equivalently, i.e., the differences in excited state energies were in the same range, and in line with the experimental data, although the absolute transition energies were too high. Although the MR-MP2 method came closest to the experimental values for **1**, the difference between the first and second excited state energies for **2** was significantly lower than the experimental value. The relative excitation energies calculated with the MRDCI and MR-MP3 method were in line with the experimental data. It can therefore be concluded that the MR-MP2 method erroneously describes the lowest valence transitions at least in the oligo(cyclohexylidene) series. The application of the MRDCI method for the calculation of the excited states of **1** and **2** is justified despite the lack of electron correlation by freezing too many orbitals. This is especially promising, taking into consideration the newly developed MRDCI codes [13–15], which will be more effective and which can be used for handling even larger molecules.

Acknowledgements

References

[1] M. Allan, P.A. Snyder, M.B. Robin, J. Phys. Chem. 89 (1985) 4900.

[2] F.J. Hoogesteger, R.W.A. Havenith, J.W. Zwikker, L.W. Jenneskens, H. Kooijman, N. Veldman, A.L. Spek, J. Org. Chem. 60 (1995) 4375.

[3] P.A. Snyder, L.B. Clark, J. Chem. Phys. 52 (1970) 998.

[4] A. Yogev, J. Sagiv, Y. Mazur, J. Am. Chem. Soc. 94 (1972) 5122.

[5] M.B. Robin, R.R. Hart, N.A. Kuebler, J. Chem. Phys. 44 (1966) 1803.

[6] R.J. Buenker, S.D. Peyerimhoff, W. Butscher, Mol. Phys. 35 (1978) 771.

[7] R.J. Buenker, S.-K. Shih, S.D. Peyerimhoff, Chem. Phys. 36 (1979) 97.

[8] R.J. Buenker, S.D. Peyerimhoff, Theor. Chim. Acta 35 (1974) 33.

[9] R.J. Buenker, Stud. Phys. Theor. Chem. 21 (1982) 17.

[10] R.W.A. Havenith, J.H. van Lenthe, L.W. Jenneskens, F.J. Hoogesteger, Chem. Phys. 225 (1997) 139.

[11] R.W.A. Havenith, L.W. Jenneskens, J.H. van Lenthe, Chem. Phys. Lett. 282 (1998) 39.

[12] V.R. Saunders, J.H. van Lenthe, Mol. Phys. 48 (1983) 923.

[13] R.J. Buenker, R.A. Phillips, J. Mol. Struct. THEOCHEM 123 (1985) 291.

[14] A.B. Alekseyev, H.P. Liebermann, G. Hirsch, R.J. Buenker, Chem. Phys. 225 (1997) 247.

[15] M. Hanrath, B. Engels, Chem. Phys. 225 (1997) 197.

[16] J.H. van Lenthe, P. Pulay, H.J.J. van Dam, Multi Reference Møller-Plesset Perturbation Theory Option (Fayetteville, Arkansas/Utrecht, The Netherlands), 1989–1996.

[17] K. Wolinski, H.L. Sellers, P. Pulay, Chem. Phys. Lett. 140 (1987) 225.

[18] K. Wolinski, P. Pulay, J. Chem. Phys. 90 (1989) 3647.

[19] B.O. Roos, K. Andersson, Chem. Phys. Lett. 245 (1995) 215.

[20] K. Andersson, P.-Å. Malmqvist, B.O. Roos, A.J. Sadlej, K. Wolinski, J. Phys. Chem. 94 (1990) 5483.

[21] K. Andersson, P.-Å. Malmqvist, B.O. Roos, J. Chem. Phys. 96 (1992) 1218.

[22] H.J.J. van Dam, J.H. van Lenthe, Mol. Phys. 93 (1998) 431.

[23] H.J.J. van Dam, J.H. van Lenthe, P.J.A. Ruttink, Int. J. Quant. Chem. 72 (1999) 549.

[24] M.F. Guest, J.H. van Lenthe, J. Kendrick, K. Schöffel, P. Sherwood, R.J. Harrison, GAMESS-UK, a package of ab initio programs, 1998. With contributions from R.D. Amos, R.J. Buenker, M. Dupuis, N.C. Handy, I.H. Hillier, P.J. Knowles, V. Bonacic-Koutecky, W. von Niessen, V.R. Saunders, A.J. Stone. It is derived from the original GAMESS code due to M. Dupuis, D. Spangler, J. Wendolowski, NRCC Software Catalog, vol. 1, Program No. QG01 (GAMESS) 1980.

[25] V.R. Saunders, M.F. Guest, Atmol Program Package, SERC Daresbury Laboratorium, Daresbury, UK.

[26] S.R. Langhoff, E.R. Davidson, Int. J. Quant. Chem. 8 (1974) 61.

[27] J. Verbeek, J.H. van Lenthe, P.J.J.A. Timmermans, A. Mackor, P.H.M. Budzelaar, J. Org. Chem. 52 (1987) 2955.

[28] R.J. Buenker, S.D. Peyerimhoff, Theoret. Chim. Acta (Berl.) 39 (1975) 217.

[29] H.-J. Werner, Mol. Phys. 89 (1996) 645.

[30] F.J. Hoogesteger, Oligo(cyclohexylidenes). Development of Novel Functional and Organized Materials, Ph.D. Thesis, Utrecht University, The Netherlands, 1996.

[31] H.J.J. van Dam, J.H. van Lenthe, Mol. Phys. 90 (1997) 1007.