Ab initio study of the structure and dipole moment of azulene

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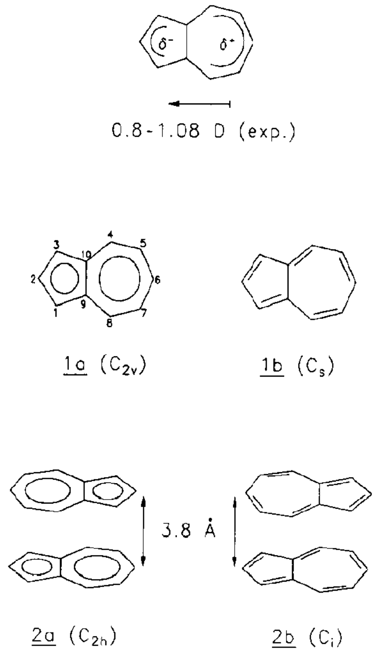
The two structures of azulene with C_{2v} and C_s symmetry, their energy difference and their dipole moments have been investigated via ab initio quantum mechanics. Self-consistent-field (SCF) theory was used in conjunction with various basis sets up to TZP+f quality. The SCF method fails to predict the correct minimum energy structure (C_s instead of C_{2v}) due to the neglect of electron correlation. MP2 wavefunctions were used to analyze different correlation contributions which reduce the SCF value of the dipole moment μ by ≈ 0.5 D. The application of the MR-SDCI method yields $\mu = 0.93$ D in good agreement with the experimental value ($\mu_{exp} = 0.79$ D). The results are discussed by means of perturbation theory. Additionally, the azulene "sandwich" dimer was investigated at several internuclear distances to explore the origin of the disordered crystal structure.

1. Introduction

The azulene molecule has been of longstanding interest to theoretical chemists due to its unusual physical properties [1–3]. While azulene (**1**) and naphthalene are structurally similar benzoid isomers containing ten π electrons, their properties are distinct in a number of respects [4]. The non-alternant azulene molecule is a blue-coloured compound which shows a large dipole moment (for a hydrocarbon) of $\mu = 0.8$–1.08 D [#1] [5,6] and has interesting photophysical properties (e.g. $S_2 \rightarrow S_0$ fluorescence [7], large hyperpolarizability [8]) which have stimulated many theoretical studies [3,9–13]. Furthermore, this molecule has been considered as a test compound in the development of theories of aromaticity [3,11,14,15]. This is not surprising if one looks at the generally accepted explanation for the observed dipole moment, which is attributed to a partial charge transfer from the seven-membered to the five-membered ring (compare scheme 1). In the limit of the transfer of one unit charge there exists a resonance structure which formally obeys the Hückel $4n+2$ rule of aromatic stability in both rings ($n=1$). Theoretically this partial charge transfer has been confirmed by means of population analysis [1,2] and with the shift of the carbon 1s orbital energies, which is related to the difference in the valence electron distributions [9].



Scheme 1.

Surprisingly most theoretical treatments cannot

[#1] 1 D = 3.336×10^{-30} C m.

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adequately describe the electronic wavefunction of azulene; generally the result is an overestimation of the calculated value of the dipole moment (Hückel-MO: 6.9 D [1], CNDO: 3.1 D [8] ab initio SCF, STO-3G: 1.81 D [12], ab initio SCF, 6-31G: 1.73 D [12]). The best value for μ reported to date was calculated with the inclusion of electron correlation by second-order Møller–Plesset perturbation theory [16] (6-31G basis set) yielding 1.23 D [12], which is far from the best gas-phase value of 0.79 ± 0.01 D (Stark-effect measurements [5]). The frequently cited value of 1.08 D [6] determined in benzene solution seems to be an overestimate due to several assumptions made during its evaluation. From the results of SCF calculations it was concluded that the dipole moment arises from the π system only [11], while HOMO→LUMO excited configurations in the MP2 treatment effectively transfer charge density back, reducing the calculated value obtained at the SCF level [12]. Up to now no attempts have been reported to reduce the difference between the experimental and theoretical values.

Obviously there is also some controversy in the literature about the geometric structure of the molecule [3,11,12,17,18]. Usually it is assumed that azulene prefers a structure with equalized C–C bond lengths along the perimeter (C_{2v} symmetry **1a**, see scheme 1) instead of the bond alternating structure with C_s symmetry (**1b**, see scheme 1). No conclusive experimental result has confirmed this assumption, since the analysis of the X-ray data is complicated due to the disordered crystal structure [19]. Theoretically, this question is also important for the calculation of μ since a difference of ≈ 0.5 D is evaluated at the SCF level for structures **1a** and **1b** [12], the value of μ for structure **1b** being lower (i.e. nearer to the experimental value). The theoretical predictions for the minimum energy structure reported in the literature are also not decisive. Geometry optimizations at the semi-empirical (MNDO [17]) or STO-3G level [12] result in a bond alternating structure, although the energy difference $\Delta E = E(1\mathrm{b}) - E(1\mathrm{a})$ is small [12] (≈ -3 kcal/mol, the C_s structure being more stable). Increasing the AO basis to 6-31G and the inclusion of electron correlation seems to stabilize the bond-equalized perimeter with C_{2v} symmetry, but a conclusive decision has not been reached [12].

In this work high-quality ab initio calculations with full geometry optimization using extended basis sets up to TZP quality including f functions at the carbon atoms are presented. Correlated wavefunctions at MP2 and MR-SDCI levels of sophistication are evaluated for both structures. These partitioned into the contributions of the σ and π electrons in order to gain deeper insight into the origin of the dipole moment and into the structural preferences of azulene. Furthermore, the effect of the crystal forces on the minimum energy structure of azulene is considered using the dimers **2a** and **2b** (see scheme 1) as model systems.

2. Theoretical details

Self-consistent-field (SCF) theory using the standard Gaussian basis sets 3-21G [20], 6-31G, 6-31G* [21], DZP [22], TZP [23,24] and TZP+f (as TZP, additional f functions with exponent 0.75 at the carbon atoms) were used to obtain initial values for the energy differences between the two structures **1a** and **1b**. The ab initio SCF and MP2 calculations and the SCF geometry optimizations were carried out with the TURBOMOLE program package [25]. Complete geometry optimization of all geometrical parameters within the constraint of C_{2v} (**1a**) or C_s (**1b**) symmetry were performed with basis sets up to TZP quality. MP2 geometry optimizations were done with the GAUSSIAN 90 program [26]. The energies of the dimers **2a** and **2b** were evaluated using the TZP optimized geometries arranged similarly as observed in the crystal structure at intermolecular distances of 3.5–4.0 and 10 Å. The dipole moments in the MP2 approach were calculated using the finite differences of the MP2 energies in the presence of an electric field of 0.001 au (estimated accuracy: ±0.001 D). Multireference CI calculations (MR-SDCI) were undertaken in the standard manner of Buenker and Peyerimhoff [27,28] using Hartree–Fock (HF) MOs of the ground-state wavefunction as the molecular basis. The calculated dipole moments and correlation energies refer to the largest CI secular problem solved (i.e. no extrapolation technique was applied). In all calculations the three configurations (see section 3.2) with the largest coefficient contributions to the ground-state wavefunction were used as reference configurations. The threshold T in the selection of spin-adapted configurations (SAFs) based on perturbation theory was varied from $T=5$ μhartree to $T=0.1$ μhartree.

3. Results and discussion

3.1. Structure and energetics

The geometry optimization of the two azulene structures employing the respective symmetry constraints (C_{2v} **1a**, C_s **1b**) was first carried out at the SCF level. To obtain conclusive results at this level of approximation, extended basis sets up to TZP quality were used (see table 1). The geometries (e.g. the C–C bond lengths) as obtained with the TZP basis will be discussed and are shown together with the X-ray data (obtained assuming C_{2v} symmetry) reported by Robertson et al. [19] in fig. 1. Except for the 6-31G basis (see below) the geometrical parameters obtained with the different basis sets are similar (bond lengths agree to within 0.005 Å, bond angles to within 2°). As expected, structure **1b** shows strong bond alternation along the perimeter, the formal double bonds ranging from 1.353 to 1.363 Å, the single bonds being 1.418 to 1.431 Å long. In contrast, all C–C bond lengths of **1a** are nearly equal ranging from 1.383 to 1.395 Å. The length of the bridging bond (C9–C10) is remarkably long in both structures (1.484 Å), which is essentially the estimated single bond distance between sp^2-hybridized carbon atoms (1.48–1.50 Å [2]). Comparison of the calculated and experimental bond lengths shows a good, but somewhat fortuitous agreement for the C_{2v} structure **1a**, since the X-ray data were interpreted assuming this molecular symmetry.

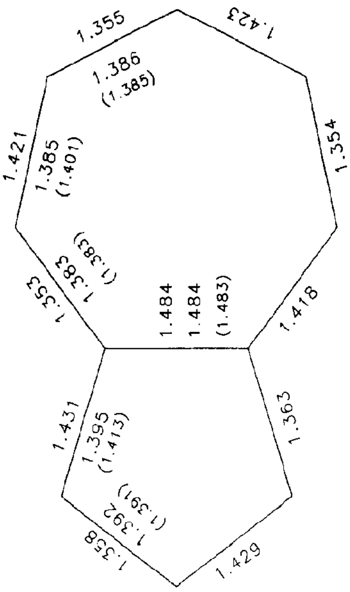

Fig. 1. Bond lengths of the SCF optimized geometries (TZP basis set) of the C_{2v} structure **1a** (values inside the rings) and the C_s structure **1b** (outer values). The experimental data of the X-ray analysis (assuming C_{2v} symmetry [19]) are given in parentheses.

The results obtained with the 6-31G basis set need some special consideration since no stationary point with C_s symmetry was found in the optimization process employing this AO basis. Instead, an increase of the molecular symmetry to C_{2v} was ob-

Table 1
Total SCF energies of **1a**, energy differences ($\Delta E=E(\mathbf{1b})-E(\mathbf{1a})$) to the structure **1b** and dipole moments (μ) calculated with different AO basis sets and full geometry optimization

Method	E(**1a**) (au)	ΔE (kcal/mol)	μ (**1a**) (D)	μ (**1b**) (D)
3-21G [a]	−381.13780	−0.06	1.678	1.585
6-31G [b]	−383.14729	<0.01	1.736	1.728
6-31G* [a]	−383.28060	−0.35	1.530	1.316
DZP	−383.26811	−0.26	1.556	1.366
TZP	−383.36511	−0.40	1.564	1.322
TZP+f [c]	−383.38070	−0.32	1.537	1.298

[a] The structure with C_{2v} symmetry (**1a**) was characterized as a saddle point by one imaginary vibrational frequency (6-31G*: $\nu_i=600$ cm^{-1}).

[b] No stationary point with C_s symmetry was found. The geometry optimization converges to the C_{2v} structure.

[c] These values were calculated using the TZP optimized geometry.

served. The results, as obtained with the larger basis sets show however, that approaching the Hartree–Fock limit both structures represent stationary points on the azulene hypersurface. Therefore, previous ab initio investigations of the azulene structure [12] based on calculations using the 6-31G basis set are indecisive. It seems clear that missing polarization functions yield an insufficiently flexible wavefunction for the azulene molecule. With the poor 3-21G basis a fortuitous cancellation of errors occurs and thus nearly identical geometrical parameters compared to the extended basis sets are obtained.

The two structures **1a** and **1b** as obtained with the 3-21G and 6-31G* basis sets were also characterized by an analytical calculation of the harmonic force constant matrix. In both calculations one imaginary vibrational frequency was obtained for the C_{2v} structure, representing a saddle point for the valence tautomerization of azulene. Contrarily, the C_s structure corresponds to a local minimum showing only real vibrational frequencies. Since two (identical) C_s structures are possible (related by a mirror-plane) this situations corresponds to a double-minimum potential (DMP) along the $C_s \rightarrow C_{2v} \rightarrow C_s$ coordinate. Due to the size of the azulene molecule, force constant calculations are not feasible with the extended basis sets. However, the similarities of the calculated nuclear geometries and energy differences (see below) indicate that the characteristics of the stationary points remain as the Hartree–Fock limit is approached.

In order to evaluate the effect of electron correlation (a detailed discussion is given below) on the minimum energy geometry, MP2 optimizations using the 3-21G and 6-31G basis sets were performed. Compared to the SCF results the observed C_{2v} structures show a large lengthening of all C–C bonds (average increase with the 6-31G basis: 0.026 Å). With both basis sets the initial structures with alternating bond lengths were equalized to C_{2v} symmetry. The reliability of the structures is estimated by comparison of the calculated and experimental moments of inertia as obtained at the best SCF (TZP basis) and at the MP2/6-31G level (see table 2). As expected the values as evaluated from the SCF geometries are too small (the whole molecule is calculated to be too compact) while the reverse is true for the MP2 geometry. However, the agreement is better for the SCF geometries which may be attributed to the missing d functions in the MP2 calculation. Thus, the SCF/TZP optimized structures are adopted as the most reliable approach to the "true" azulene geometry.

The energy differences between **1a** and **1b** (see table 1) are calculated to be around −0.3 kcal/mol, i.e. the bond alternating structure **1b** is more stable. The employment of basis sets larger than 6-31G* does not alter the ΔE value significantly. Although it should also be mentioned that such small ΔE values are only meaningful to test the performance of the SCF approximation since they are of the same order of magnitude as compared to the zero-point energy (ZPE) corrections ($\Delta E_{ZPE} = 2$ kcal/mol) and to the thermal energy at 300 K (0.6 kcal/mol). The ΔE values presented here are considerably higher (−0.3 versus ≈ -3 kcal/mol) than previous ab initio data reported using STO-3G or MINDO/3 geometries [12]. This suggests that standard geometries are not sufficient for the calculation of small energy differences, an observation which has been reported for other benzoid hydrocarbons [18].

3.2. Dipole moment

Previous experience with smaller basis sets has shown that the calculated values of the dipole mo-

Table 2
Comparison of calculated and experimental moments of inertia (I) of azulene (in 10^{-47} kg m^2)

	TZP/SCF (**1a**)	TZP/SCF (**1b**)	6-31G/MP2 (**1a**) [a]	Exp. [b]
I_A	290.08	290.79	302.15	295.38
I_B	659.71	661.96	685.53	668.96
I_C	949.78	952.76	987.68	964.09

[a] No stationary point with C_s symmetry was found. The MP2 geometry optimization converges to the C_{2v} structure.
[b] Ref. [5].

ment of **1** are generally overestimated by the SCF method. Inspection of table 1 confirms this finding, however a decrease in the values of μ (pointing from the seven-membered towards the five-membered ring) for both structures with increasing AO basis is observed. The d functions centered at the carbon atoms have a significant effect on the results while additional f functions only slightly decrease the calculated values of the dipole moment. Values of 1.5 (**1a**) and 1.25 D (**1b**) can be estimated to be near the HF limit. The higher value of μ obtained for the bond-equalized structure **1a** is understandable due to a more "aromatic" character in both rings, a situation which is favoured by a larger amount of charge transfer. The component of the dipole moment perpendicular to the long molecular axis (y) of the C_s structure is calculated to be $\mu_y^2 = 0.03$ D^2. Comparison with the experimental value of $\mu_y^2 = 0.08 \pm 0.09$ D^2 [5] shows that the presence of a secondary symmetry plane (i.e. C_{2v} versus C_s) is not deducible from these data.

The SCF results presented so far seem to indicate that azulene has a bond alternating structure with a low barrier for the valence tautomerization. The lower value of μ calculated for structure **1b** seems to support this finding although a large difference of 0.45 D to the experimental value remains. It is well known that the SCF approximation often fails in the interpretation of the structures and energetics of large conjugated π systems due to the neglect of electron correlation [12,29]. In order to evaluate this effect in detail various treatments accounting for this were employed. The TZP optimized geometry and the 6-31G* basis set were used. This basis set (156 contracted AO functions) gives reasonable results at the SCF level and is also practicable in the calculation of correlated wavefunctions. The results of MP2 and MR-SDCI calculations are summarized in table 3. The MP2 results are partitioned into the contributions of the σ, π and σ–π interactions as evaluated from the MP2 pair energies. The correlation of the π electrons has two obvious effects, namely the increase in the stability of the C_{2v} structure ($\Delta E > 0$) and the decrease of the calculated dipole moment. The σ–π correlation contributions show the same trend, while the correlation of the σ electrons is negligible in the evaluation of both properties. The value for the dipole moment of **1a** is reduced with the MP2/π-treatment by ≈ 0.3 D through a back transfer of π-electron density from the five to the seven-membered ring.

The lowering of μ in the MP2 treatments is generally larger for structure **1a** than for **1b**. In a simple MO diagram this result can be explained with the increased spacing of the highest π MOs in the C_s structure (see fig. 2). The main contributions to the HF configuration ψ_0 of **1a** are the doubly excited configurations ψ_1–ψ_3

$$\psi_0 = \ldots 3b_1^2 2a_2^2 ,$$

$$\psi_1 = \ldots 3b_1^1 2a_2^1 4b_1^1 3a_2^1 ,$$

Table 3

Correlation energies of **1a**, energy differences ($\Delta E = E(1b) - E(1a)$) to the structure **1b** and dipole moments (μ) calculated with various treatments. The SCF-TZP optimized geometries and the 6-31G* basis set (156 AOs) were employed

Method	E_{corr}(1a)	ΔE_{corr} (kcal/mol)	ΔE_{tot} (kcal/mol)	μ (1a) (D)	μ (1b) (D)
SCF	–	–	−0.34	1.522	1.283
MP2/π [a]	−0.14095	1.61	1.27	1.208	1.104
MP2/σ [b]	−0.65052	−0.20	−0.54	1.535	1.296
MP2/σ–π [c]	−0.47242	2.87	2.53	1.336	1.286
MP2/full val. [d]	−1.26388	4.28	3.94	1.036	1.121
MR-SDCI/π [e]	−0.15336	1.54	1.20	0.929	0.824

[a] 10 π electrons were correlated in all π MOs (40).

[b] 38 σ electrons were correlated in all σ MOs (106).

[c] Sum of MP2 pair energies involving one σ and one π MO.

[d] The carbon 1s MOs were kept doubly occupied.

[e] 10 π electrons were correlated in all π MOs (40). Details of MR-SDCI calculation: Selection threshold 1×10^{-7} au; 4 reference configurations (see text); **1a**: 57645 SAFs total, 20890 selected; **1b**: 115031 SAFs total, 26436 selected.

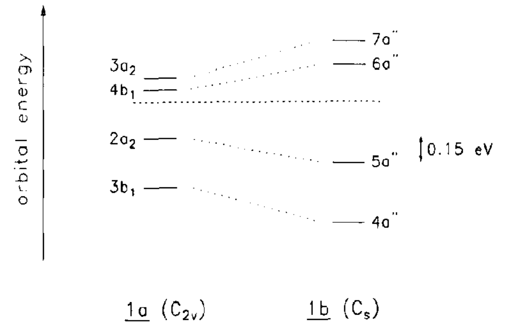

Fig. 2. Schematic orbital correlation diagram of the two highest occupied and two lowest unoccupied π MOs of the azulene structures **1a** and **1b**.

$$\psi_2 = \ldots 3b_1^0 2a_2^2 4b_1^2 ,$$

$$\psi_3 = \ldots 3b_1^2 2a_2^0 3a_2^2 ,$$

which involve excitations between the two highest occupied and two lowest virtual π MOs. The configurations ψ_1–ψ_3 are mainly responsible for the back transfer of charge mentioned above. The increased spacing of the analogous MOs in the C_s structure increases the energy of these configurations which results (using perturbation theory) in a lower contribution to the leading HF configuration. Similar arguments can be applied in the explanation of the lower correlation energy of **1b** which results in a stabilization of the C_{2v} isomer by ≈4 kcal/mol (MP2/full valence electron treatment). Again the π and σ–π contributions to the MP2 energy difference dominate. From the ΔE_{tot} value of 3.94 kcal/mol at the MP2 level it is deduced that the SCF-DMP (with the C_{2v} structure at the top of the barrier) is an artefact of the single determinant approximation. The results of the MP2 optimizations also suggest that only the C_{2v} structure is a stationary point on the azulene hypersurface when electron correlation is taken into account.

The reliability of the MP2 results was checked by MR-SDCI/π calculations using the four reference configurations ψ_0–ψ_3 given above. Test calculations have shown that threshold values $T < 1$ μhartree were needed to obtain stable results for the calculated dipole moment. Unfortunately such small values of T prohibits the inclusion of the σ electrons in the MR-SDCI treatment due to a large increase in the number of selected SAFs ($>10^5$). The ΔE_{corr} value obtained with the MR-SDCI/π treatment is nearly identical to the MP2/π result whereas the value of μ is reduced by ≈0.3 D for both structures. Assuming that the neglected σ–π contribution in the MR-SDCI treatment is ≈0.2 D (estimated from the difference $\mu(\text{SCF}) - \mu(\text{MP2}/\sigma\text{–}\pi)$) a final value of $\mu = 0.7$–0.8 D for **1a** is obtained which is in good agreement with the experimental value of $\mu_{exp} = 0.79 \pm 0.1$ D. The slight underestimation might be attributed to the relative small AO basis used (6-31G*). The sum of weights of the doubly excited reference configurations in the MR-SDCI/π wavefunctions ψ_1–ψ_3 are 0.068 (**1a**) and 0.038 (**1b**) respectively which demonstrates the applicability of the perturbation theory arguments given above.

3.3. The azulene dimer

The results presented so far clearly show that electron correlation is largest in the bond-equalized structure **1a** which is certainly the energy minimum of an isolated azulene molecule. Considering the problems associated with the analysis of the disordered crystal structure [19] it seems interesting to evaluate the crystal forces theoretically. As model systems the "head to tail" dimers **2a** (see scheme 1, bond equalized, C_{2h} symmetry) and **2b** (bond alternating, C_i symmetry) were used. The primary question is obviously whether the preference for the C_{2v} structure is retained in the dimer. Besides this, the SCF and MP2 energies calculated at different intermolecular distances give an insight into the intermolecular forces between the two molecules and their origin (dipole–dipole or dispersion forces). The results are summarized in table 4.

First it is noted, that the bond alternating dimer **2b** is more stable at the SCF level while the opposite is found at the MP2 level. The energy differences increase with decreasing intermolecular distance *r*. The energetic proportions between the structural isomers calculated at both theoretical levels are qualitatively analogous to those in the monomers. Assuming that the intermolecular forces between the two molecules are larger than the forces between the elementary cells (containing two molecules) the preference for a bond equalized structure in the crystal could be deduced.

Considering the total energy of **2a** as a function of

Table 4
Total energies of the dimer **2a** ($C_{2v}\rightarrow C_{2h}$) and energy differences ($\Delta E = E(2b) - E(2a)$) to the dimer **2b** ($C_s\rightarrow C_i$) at SCF and MP2 [a] levels of theory calculated at different internuclear distances. The TZP optimized geometries and the 6-31G* basis set were employed

R (Å)	E_{SCF}(2a) (au)	E_{MP2}(2a) (au)	ΔE_{SCF} (kcal/mol)	ΔE_{MP2} (kcal/mol)
3.5	−766.54664	−767.96161	−1.35	7.02
3.8 [b]	−766.55542	−767.96335	−0.92	6.89
4.0	−766.55792	−767.96156	−0.79	6.82
10.0	−766.56099	−767.95515	−0.67	6.79

[a] All MOs with $\epsilon < -0.7$ au were kept doubly occupied.

[b] The interaction energy of **2a** at 3.8 Å is + 3.5 kcal/mol at the SCF and − 5.2 kcal/mol at the MP2 level. The counterpoise correction (SCF) for the BSSE error is 1.5 kcal/mol which yields an upper limit for the total binding energy of $E_b = -2$ kcal/mol.

r it is seen that the SCF potential curve is totally repulsive. Contrarily, the MP2 energy has a minimum around 3.8 Å, which is in good agreement with the experimentally observed distance of 3.8–3.95 Å [19]. Similar theoretical results have been reported for the sandwich dimer of benzene [30] which demonstrates that the interaction of the two dipoles in the azulene dimer is negligible and dispersion forces dominate. The uncorrected binding energy at the MP2 level is $E_b = -5.2$ kcal/mol. Due to the size of the molecular system the basis set superposition error (BSSE) could only be calculated (counterpoise correction) at the SCF level, yielding 1.5 kcal/mol. Assuming that the BSSE correction is twice as large in the MP2 calculation [31] an interaction energy of $E_b \approx -2$ kcal/mol can be estimated which is larger than the corresponding value obtained for the benzene dimer ($E_b = -0.26$ kcal/mol at $r = 4.0$ Å [30]).

4. Conclusions

The results of the present ab initio investigation leave little doubt that the bond-equalized structure with C_{2v} symmetry is the only minimum on the azulene hypersurface. The single determinant approach wrongly predicts a double-minimum potential curve with the C_s structure at the minimum. Furthermore, with the HF method the calculated dipole moment is in error by ≈0.7 D. Both defects remain as the HF limit is approached and are attributed to the neglect of electron correlation. The correlated MR-SDCI/π wavefunction gives a value for the calculated dipole moment of 0.93 D which is in better agreement with the experimental value of $\mu_{exp} = 0.79 \pm 0.1$ D. The remaining difference is attributed to the neglect of the effect of σ–π electron correlation which is estimated to be ≈ −0.2 D. The MP2 calculations furthermore suggest that the σ–σ electron correlation effects are negligible. The origin of the disordered crystal structure remains unclear. The calculations of the sandwich dimers have clearly shown that the structural preference for the bond-equalized structure is retained at various intermolecular distances. Jet-spectroscopic studies could probably be helpful in evaluating accurate structural information and dimer binding energies which are comparable to the theoretical predictions of $E_b \approx -2$ kcal/mol (at $r = 3.8$ Å). This is of particular importance since the ab initio results suggest a minor contribution of dipole–dipole interactions for the attractive part of the intermolecular potential.

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