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Published on Web 07/17/2003

Ab Initio Calculation of the Vibrational and Electronic Spectra of *trans*- and *cis*-Azobenzene

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Abstract: We report accurate geometries and harmonic force fields for *trans*- and *cis*-azobenzene determined by second-order Møller−Plesset perturbation theory. For the trans isomer, the planar structure with C_{2h} symmetry, found in a recent gas electron diffraction experiment, is verified. The calculated vibrational spectra are compared with experimental data and density functional calculations. Important vibrational frequencies are localized and discussed. For both isomers, we report UV spectra calculated using the second-order approximate coupled-cluster singles-and-doubles model CC2 with accurate basis sets. Vertical excitation energies and oscillator strengths have been determined for the lowest singlet $n\pi^*$ and $\pi\pi^*$ transitions. The results are compared with the available experimental data and second-order polarization propagator (SOPPA) and density functional (DFT) calculations. For both isomers, the CC2 results for the excitation energies into the S_1 and S_2 states agree within 0.1 eV with experimental gas-phase measurements.

1. Introduction

During the past decade, an increasing interest in azobenzene dyes emerged, accompanied by research activities in various fields. The reason for this is that polymer films with azobenzene dyes in their side chains are found to be promising materials for digital data storage.[1−3] The storage process exploits the photochemical reactivity of azobenzenes and their capability to undergo reversible cis/trans isomerizations. The understanding of the latter process requires a reliable model for the ground and the lowest excited states of azobenzenes and their optical properties. Quantum chemical calculations will be of valuable help for this, if able to describe accurately the electronic structure of the states involved in the photochemical process. A recent ab initio study using the second-order polarization propagator approximation (SOPPA) could reproduce the experimentally observed trends for shifts of the lowest singlet excitations upon substitution[4] but was found to give unreliable results for the absolute values of the vertical excitation energies and the separation of the individual states.[5] One reason for this was the use of nonoptimized geometries and of rather small basis sets, which allowed only a qualitative but not a quantitative description of the electronic structure.

The purpose of the present communication is to provide accurate ab initio data for the equilibrium geometry and the vertical excitation energies of *trans*- and *cis*-azobenzene. To achieve this, we used second-order Møller−Plesset perturbation theory (MP2) and the second-order approximate coupled-cluster singles-and-doubles model CC2 together with large basis sets, which give results close to the basis set limit of these methods. Higher-order correlation effects on the vertical excitation energies are estimated by coupled-cluster singles-and-doubles (CCSD) calculations in a small atomic natural orbital (ANO) basis set. Also, density functional (DFT) methods were employed for both equilibrium geometries and excitation energies but found to be inferior to the former methods. The results of the present MP2/cc-pVTZ and CC2/aug-cc-pVTZ calculations should provide a reliable comparison for investigations of the effects of substitution on geometry, optical properties, and photochemical reactivity and can serve as benchmarks for more approximate calculations on azobenzenes and a better understanding of experimental measurements of the structure and the vibrational and electronic spectra of these molecules.

2. Computational Details

If not mentioned otherwise, all calculations presented in the following were carried out with the TURBOMOLE program package.[6−8] The equilibrium structures of *trans*- and *cis*-azobenzene were optimized at the MP2 level using the cc-pVTZ basis.[9,10] A frozen core approximation ($1s^2$ at C and N) was employed, and the resolution-of-the-identity (RI) variant of MP2[11] was used to make the calculations feasible. Triple-ζ basis sets, as the cc-pVTZ basis, give MP2 geometries and harmonic frequencies close to the basis set limit. Larger basis sets usually do

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10.1021/ja034433o CCC: $25.00 © 2003 American Chemical Society

not lead to more accurate results since the remaining error is then dominated by higher-order electron correlation contributions.[12] The harmonic force fields were obtained by numerical differentiation of the RI-MP2 gradient using the same basis sets; infrared intensities were calculated using the double harmonic approximation.[13]

The vertical excitation energies were calculated at the optimized MP2/cc-pVTZ equilibrium structures using the CC2[14] model. The latter is an approximation to CCSD, which gives excitation energies for single excitations correct through second order in the electron fluctuation potential. It is best understood as part of the hierarchy CCS, CC2, CCSD, CC3, ...[15] If the wave function of the excited state is dominated by single replacements out of the reference determinant, CC2 gives vertical excitation energies typically correct within 0.3 eV.[15,16] For these calculations, again the frozen core and the resolution-of-the-identity approximation (RI-CC2[17]) were used. The calculations were carried out in the aug-cc-pVTZ basis sets.[9,10,18] These are expected to give for the investigated states excitation energies close to the CC2 basis set limit, since calculations in the aug-cc-pVDZ basis showed that already the changes from DZ to TZ are modest. To estimate the effect of higher-order correlation contributions, we performed CC2 and CCSD calculations in a small [3s2p1d/2s] contraction of the ANO basis set by Widmark et al.[19] These calculations were carried out with the Dalton program package.[20]

For the RI approximation, the auxiliary cc-pVTZ and aug-cc-pVTZ basis sets from ref 21 were used. With these, the error introduced by the RI approximation in MP2 and CC2 is negligible,[21,22] while such calculations are about an order of magnitude faster than conventional MP2 and CC2 calculations and thus make it possible to apply MP2/cc-pVTZ and CC2/aug-cc-pVTZ to molecules with more than 10 non-hydrogen atoms.

For the DFT calculations on the harmonic frequencies, we used the BP86 functional[23,24] and TZVP[25,26] basis sets and equilibrium structures obtained with the same functional and basis sets. These calculations were carried out using the DFT programs reported in ref 27−29 and the analytic second derivative program AOFORCE[30] and employed the RI-J approximation.[28] The DFT-BP86 calculations for the excitation energies were performed with the ESCF program[31−36] using a TZVP basis set augmented by a (1s1p2d2f/1s2p2d) set of primitive functions with the exponents taken from the most diffuse functions of the aug-cc-pVTZ basis. This basis set is in the following denoted "aug-TZVP". For the RI-J approximation, we used the TZVPP fitting basis.[26] These calculations were carried out at the DFT-BP86/TZVP optimized equilibrium structures.

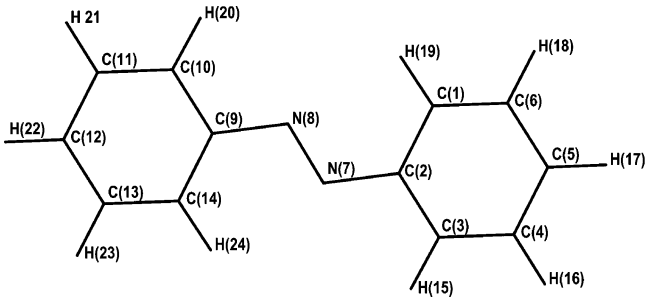


Figure 1. *trans*-Azobenzene (TAB).

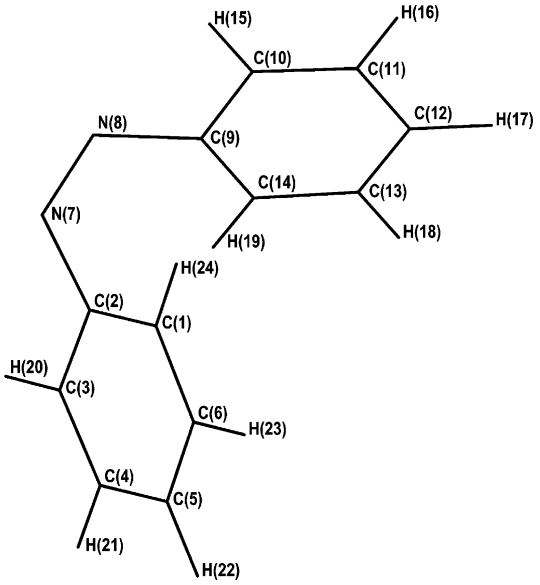


Figure 2. *cis*-Azobenzene (CAB).

3. Structures

The structures of *trans*- and *cis*-azobenzene are shown in Figures 1 and 2. The MP2/cc-pVTZ results for the equilibrium geometries are given in Tables 1 and 2 in comparison with the available experimental data[37−39] and DFT-BP86/TZVP results. The structure of the trans isomer has been the object of some discussion in the literature, since first X-ray diffraction results[38,40] suggested that *trans*-azobenzene is planar with C_{2h}

(10) Extensible computational chemistry environment basis set database, version 1.0, as developed and distributed by the molecular science computing facility, environmental and molecular sciences laboratory which is part of the Pacific Northwest Laboratory, P.O. Box 999, Richland, Washington 99352, USA, and funded by the U.S. Department of Energy. PNL is a multiprogram laboratory operated by Battelle Memorial Institute for the U.S. Department of Energy under Contract de-ac06-76rlo 1830.
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Table 1. Geometry of *trans*-Azobenzene[a]

	MP2 cc-pVTZ	DFT-BP86 TZVP	expt (GE)[37]	expt (X-ray)[38]
	Bond Lengths, pm			
$N^{(7)}-N^{(8)}$	126.8	126.7	126.0(8)	124.7
$C^{(2)}-N^{(7)}$	141.7	142.0	142.7(8)	142.8
$C^{(2)}-C^{(3)}$	139.7	140.5	140.1	138.9
$C^{(2)}-C^{(1)}$	140.0	140.9	140.5	138.7
$C^{(3)}-H^{(15)}$	108.1	109.1	110.2(7)	
$C^{(1)}-H^{(19)}$	108.0	109.0	110.2(7)	
	Angles, deg			
$C^{(2)}-N^{(7)}-N^{(8)}$	113.7	114.8	113.6(8)	
$C^{(3)}-C^{(2)}-N^{(7)}$	115.1	115.3		115.6
$C^{(1)}-C^{(2)}-N^{(7)}$	124.6	124.8		123.7
$C^{(1)}-C^{(2)}-C^{(3)}$	120.3	119.8		120.7
$C^{(2)}-C^{(1)}-C^{(6)}$	119.3	119.6		119.1
$C^{(2)}-C^{(3)}-C^{(4)}$	120.1	120.2		119.6
$C^{(2)}-C^{(3)}-H^{(15)}$	118.3	118.2		
$C^{(2)}-C^{(1)}-H^{(19)}$	119.1	118.8		

[a] Selected bond lengths and angles of the MP2/cc-pVTZ equilibrium geometry in comparison to experimental data[37,38] and DFT-BP86/TZVP results. The experimental error is given in parenthesis. The dihedral angle C−N−N−C is 180°; the point group is C_{2h}.

Table 2. Geometry of *cis*-Azobenzene[a]

	MP2 cc-pVTZ	DFT-BP86 TZVP	expt[b] X-ray
	Bond Lengths, pm		
$N^{(7)}-N^{(8)}$	126.1	125.5	125.3
$C^{(2)}-N^{(7)}$	143.2	143.7	144.9
$C^{(1)}-C^{(2)}$	139.7	140.6	138.5
$C^{(2)}-C^{(3)}$	139.4	140.5	141.0
$C^{(1)}-C^{(6)}$	139.1	139.5	137.7
$C^{(5)}-C^{(6)}$	139.4	140.0	138.9
$H^{(24)}-C^{(1)}$	108.1	109.0	
$H^{(23)}-C^{(6)}$	108.1	109.2	
	Angles, deg		
$C^{(2)}-N^{(7)}-N^{(8)}$	120.8	124.1	121.9
$C^{(3)}-C^{(2)}-N^{(7)}$	117.0	116.4	117.3
$C^{(1)}-C^{(2)}-N^{(7)}$	122.2	122.9	122.5
$C^{(3)}-C^{(4)}-C^{(5)}$	120.0	120.1	121.7
$C^{(4)}-C^{(5)}-C^{(6)}$	119.8	119.8	119.0
$H^{(24)}-C^{(1)}-C^{(2)}$	119.9	119.9	
$H^{(20)}-C^{(3)}-C^{(2)}$	118.9	118.7	
	Dihedral Angles, deg		
$C^{(2)}-N^{(7)}-N^{(8)}-C^{(9)}$	7.3	11.4	8.0
$N^{(7)}-N^{(8)}-C^{(9)}-C^{(14)}$	53.6	48.4	53.3

[a] The MP2/cc-pVTZ equilibrium geometry in comparison to experimental[39] and DFT results. The point group is C_2. [b] Reference 39. The estimated standard deviation in the distances between non-hydrogen atoms is 0.3−0.4 pm, and that in angles involving carbon or nitrogen atoms is 0.3°.

symmetry while a later reinvestigation[41] showed that the symmetry of *trans*-azobenzene in the crystal is only C_i. On the other hand, early gas electron diffraction (GED) measurements[42] indicated that in the gas phase the geometry is slightly nonplanar with C_i symmetry. A very recent GED measurement by Tsuji et al.,[37] however, led to the conclusion that the structure in the gas phase is planar with C_{2h} symmetry. Possibly, the equilibrium structures differ between the solid state and the gas phase. In a recent communication, Hättig and Hald[5] also obtained a planar structure with C_{2h} symmetry from an MP2/cc-pVTZ optimization but did not verify, by calculating the harmonic force constants, if the structure was really a minimum. This is done in the present work, and we found that the planar structure is indeed a minimum, at least in the gas phase. The lowest vibrational frequency is found at 21 cm^{-1}, for a torsion of the benzene rings. Calculations for the structure and the vibrational frequencies of *trans*-azobenzene have been reported before at the MP2/6-31G*[43] level and for DFT using different functionals.[44] The basis sets employed in these studies have, however, been too small to give conclusive results (vide infra). When the reliability of MP2/cc-pVTZ for such well-behaved organic molecules is considered, this strongly confirms the experimental result of ref 37. Further evidence comes from the vibrational spectrum (see section 4) where very good agreement is obtained for the lowest experimentally observed bands.

Of particular importance for the calculation of excitation energies is the length of the N═N double bond, since the excitations into the S_1 and S_2 states are sensitive to the electronic structure at the azo group. The MP2 result for the N═N bond length of 126.8 pm is within the error bar of the GED experiment. DFT-BP86/TZVP gives for the N═N bond length a very similar result (126.7 pm), while DFT-B3LYP/cc-pVTZ gives an almost 2 pm shorter N═N bond length (124.9 pm). For all other bond lengths, the DFT-BP86/TZVP results are 0.3−1.0 pm larger than the MP2 values. With B3LYP/cc-pVTZ, most bond lengths (apart from the N═N distance) are obtained within ±0.2 pm of the MP2 values. When the present results are compared with calculations carried out in smaller basis sets, it becomes apparent that triple-ζ basis sets are essential for an accurate description of the azo group: BP86/6-31G*[44] gives with 127.9 pm a N═N bond length which is more than 1 pm longer than the results obtained with the TZVP basis.

When comparing the ab initio results with the experimental data, one has to keep in mind that these calculations refer to the equilibrium structure (r_e), while experimental results for azobenzene are only available for the vibrationally averaged structures. This leads to an additional uncertainty of about 0.5 pm. Note that the experimental studies also had to use some results from more approximate ab initio calculations to fit all bond distances and angles to the observed data.[37,38]

Considering this, we find the experimental and the ab initio results for the C−N and C−C distances agree within the uncertainties of the calculations and the experiment. Larger deviations are only found for the C−H (1−2 pm) and the N═N (1 pm) bond lengths. However, for the latter, the experimental result carries a large uncertainty of 0.8 pm, while C−H bond lengths are in general difficult to determine experimentally, which is reflected by the large uncertainty of the GED values. The angles are described well by both methods. The largest deviations to the experimental values are about 1° for both methods.

For the structure of *cis*-azobenzene (CAB), we find similar trends. But, since the only available experimental results are from an X-ray diffraction experiment for the solid state, they do not have the same comparative quality as the GED results for the trans isomer. In general, the MP2 results for the cis isomer are expected to have the same quality as for *trans*-azobenzene. Both, MP2 and DFT give larger N═N bond lengths than those measured for the crystal. Considering the other bond

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Table 3. Vibrational Spectrum of *trans*-Azobenzene (some selected modes)[a]

	DFT-BP86			MP2			expt	
mode	ν	Δ_ν	I	ν	Δ_ν	I	ν	Δ_ν
1 b_u	82	0	2.0	87	1	1.8	86[c]	
1 a_g	216	0		225	0		218,[c] 219[b]	4[c]
2 b_g	239	4		247	4		250,[c] 251[b]	6[c]
2 b_u	516	9	24.8	524	9	17.9	521,[d] 523[c]	7,[c] 10[d]
3 b_u	532	6	5.9	538	6	3.4	527[d]	4[d]
5 a_u	525	3	8.9	553	3	13.4	543.5,[b] 544,[c] 545[d]	1,[c] 2,[d] 3[b]
6 a_u	651	0	64.6	695	1	64.9	689,[b] 690[c]	0[c,d]
7 a_u	760	0	90.0	790	1	80.6	774,[c] 776[d]	0,[d] 1[c]
5 b_u	816	7	0.6	835	8	0.4	834,[c] 836[b]	2[c]
5 a_g	912	18		931	18		913,[b] 914[c]	12.5,[b] 16[c]
8 b_g	903	0		935	0		935,[c] 938[b]	7.5,[b] 8[c]
9 a_u	906	0	7.5	940	1	7.3	926,[c] 927[d]	1,[c] 0[d]
6 b_u	988	0	3.7	1013	0	6.0	1000[c,d]	0[c,d]
7 b_u	1014	0	15.8	1041	0	15.4	1020,[d] 1021[c]	0,[d] 1[c]
8 b_u	1072	0	16.4	1098	0	12.0	1070,[c] 1072,[d] 1097[b]	12,[b] 0[c,d]
9 b_u	1140	1	33.7	1172	1	23.3	1152,[d] 1155,[c] 1158[b]	0,[d] 1,[b] 2[c]
11 a_g	1175	2		1211	4		1218,[c] 1223,[d] 1225[b]	4,[c] 10[d]
11 b_u	1218	6	18.8	1265	8	22.1	1245,[b] 1295,[c] 1300[d]	0,[d] 2[c]
12 a_g	1297	2		1330	4		1379[b]	
13 a_g	1413	32		1419	41		1439,[e] 1440,[c] 1442.5[b]	23,[c] 27,[e] 30[b]
13 b_u	1346	0	7.0	1472	0	2.6	1453,[e] 1454,[c] 1456[d]	0[c–e]
14 b_u	1443	0	12.3	1483	0	15.6	1486,[d] 1484[c,e]	1,[e] 0[c,d]
16 a_g	1479	10		1508	1		1540[b]	
15 b_u	1469	0	9.9	1515	1	10.0	1534,[d] 1560[b]	0[d]
16 b_u	1572	0	3.7	1629	1	5.0	1583,[e] 1585,[d] 1586[c]	1,[c] 0[d,e]

[a] DFT-BP86/TZVP and MP2/cc-pVTZ harmonic frequencies in comparison with experimental fundamental bands. Wavenumbers (ν) and ^{15}N isotopic shifts (Δ_ν) are in cm^{-1}, and intensities (I) are in km/mol. [b] Reference 46. Raman spectra, recorded in CCl_4. [c] Reference 47. Raman and IR spectra, recorded in solvent. [d] Reference 48. IR spectra, recorded in KBr. Experimental ^{15}N isotopic shifts for substitution of one nitrogen multiplied by two for better comparison with other experimental results and the ab initio calculations. [e] Reference 49. IR spectra, recorded in KBr.

Table 4. Vibrational Spectrum of *cis*-Azobenzene (some selected modes)[a]

	DFT-BP86			MP2			expt[b]	
mode	ν	Δ_ν	I	ν	Δ_ν	I	ν	Δ_ν
5 b	431	3	4.9	437	4	1.0	441	4
6 a	412	5	3.4	442	5	2.4	441	4
6 b	490	7	6.0	500	4	3.6	492	4
8 a	583	9	4.1	599	8	3.8	596	8
8 b	646	1	4.0	680	3	0.5	662	0
10 a	665	0	20.1	699	1	17.0	688	0
9 b	691	4	106.5	713	2	94.4	700	2
11 a	740	5	2.5	764	4	2.1		
10 b	751	4	41.0	773	4	51.8	756	4
12 a	754	3	15.6	789	3	10.3	777	4
11 b	815	10	6.4	850	1	0.7	834	0
12 b	822	6	3.6	882	13	0.8	866	12
13 b	887	1	17.9	934	6	21.6	920	0
16 a	933	0	0.1	969	0	0.2	988	0
17 b	1019	0	5.6	1045	0	4.0	1023	0
18 a	1020	0	2.8	1045	0	1.9	1023	0
18 b	1072	1	15.0	1099	1	12.3	1067	2
19 a	1074	0	1.3	1099	0	0.5	1067	2
20 a	1102	2	0.0	1166	3	0.1	1093	0
20 b	1126	2	2.5	1182	1	1.6	1152	0
23 b	1333	0	1.9	1462	0	5.0	1451	0
24 a	1504	32	52.6	1469	45	13.0	1511	50
25 a	1340	0	0.0	1473	2	3.9	1477	0
27 a	1456	11	0.5	1507	0	13.5	1575	0
25 b	1464	0	5.0	1507	0	4.4	1585	0

[a] DFT-BP86/TZVP and MP2/cc-pVTZ harmonic frequencies in comparison with experimental fundamental bands. Wavenumbers (ν) and ^{15}N isotopic shifts (Δ_ν) are in cm^{-1}, and intensities (I) are in km/mol. [b] Reference 48. IR spectra, recorded in KBr. Experimental ^{15}N isotopic shifts for substitution of one nitrogen multiplied by 2 for better comparison with other experimental results and the ab initio calculations.

lengths, we find DFT gives again larger values than MP2 and the tendency proceeds that the calculations give 1−2 pm larger bond lengths than measured experimentally. This discrepancy can only be attributed to the comparison of experimental data for the solid state with calculations for isolated molecules. When bond angles are considered, the most interesting ones are the dihedral angles for $C^{(2)}-N^{(7)}-N^{(8)}-C^{(9)}$ and $N^{(7)}-N^{(8)}-C^{(9)}-C^{(14)}$. MP2 gives for these coordinates a remarkably good agreement with the experimental results: the deviations are only 0.7° and 0.3°, respectively, while the DFT results deviate by 3.4° and 4.9°. These angles might, however, be sensitive to packing effects in the crystal. Therefore, care must be taken when comparing experimental and calculated results for these coordinates.

4. Vibrational Spectra of *trans*- and *cis*-Azobenzene

In Tables 3 and 4, we give the MP2/cc-pVTZ and DFT-BP86/TZVP results for the harmonic frequencies and intensities of *trans*- and *cis*-azobenzene for some selected modes in comparison to the available experimental data. In addition, also the ^{15}N isotopic shifts are listed. The MP2 frequencies are ordered according to increasing frequencies, while the DFT-BP86 results have been assigned such that maximum overlap with the MP2 normal coordinate was obtained. These calculations were done within the harmonic approximation for the vibrational frequencies and the double harmonic approximation for the intensities and refer to the gas phase. The deviations caused by the neglect of anharmonicities for the vibrational frequencies of the azobenzenes can be estimated roughly from the anharmonic contributions to the spectrum of benzene, which are < 140 cm^{-1} for in-plane and < 22 cm^{-1} for out-of-plane modes.[45]

4.1. Vibrational Spectrum of *trans*-Azobenzene. The absence of imaginary frequencies for the MP2/cc-pVTZ structure shows that the planar C_{2h} symmetry presents indeed a local minimum on the energy surface. Thus, the present calculations verify the result of ref 5 that MP2 gives a planar structure for *trans*-azobenzene in the gas phase, which is also corroborated by the very good agreement within a few cm^{-1} for the lowest observed vibrational frequencies. When the accuracy and reliability of MP2/cc-pVTZ calculations for structures of organic closed-shell molecules are considered, this is a strong confirmation of the experimental result of ref 37.

With a few exceptions, agreement within a few cm^{-1} is found for all bands up to 1000 cm^{-1}, that is, the out-of-plane-modes. The exeptions are a band observed at 362−368 cm^{-1},[46,47] which has no counterpart in the calculated harmonic frequencies and is probably an overtone, and three bands in the spectrum from ref 48 at 458, 659, and 813 cm^{-1}, which were not observed in the spectra recorded later and cannot be assigned to one of the MP2/cc-pVTZ harmonic frequencies.

The N═N stretching frequency, observed experimentally at ≈1440 cm^{-1}, is localized at 1413 cm^{-1} (DFT-BP86) and at 1419 cm^{-1} (MP2). For this band, we also find the largest isotopic shift upon ^{15}N substitution both in the calculations and in the experiment. Another characteristic band is the asymmetric

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Table 5. UV Spectrum of *trans*-Azobenzene[a]

	SOPPA,[4]	DFT-BP86	CC2		CCSD,[5]	
	[3s2p(1d)/2s]	aug-TZVP	aug-cc-pVTZ	%T1	extrapolated	expt
1 ^1B_g $n \rightarrow \pi^*$	2.49	2.19	2.84	94	2.95	2.82,[b] 2.95,[c] 2.80[d]
1 ^1B_u $\pi \rightarrow \pi^*$	3.90(0.61)	3.35(0.56)	4.04(0.85)	92	4.36	4.12,[b] 3.86,[c] 3.89[d]
2 ^1B_u $\pi \rightarrow \pi^*$	4.24(0.02)	3.48(0.19)	4.44(0.02)	91	4.63	
2 ^1A_g $\pi \rightarrow \pi^*$	4.25	3.46	4.45	90	4.62	
3 ^1A_g $\pi \rightarrow \pi^*$	5.07	4.16	5.15	91	5.53	
3 ^1B_u $\pi \rightarrow \pi^*$	5.82(0.27)	4.72(0.10)	5.79(0.35)	91	6.13	5.64,[b] 5.41,[c] 5.43[d]
4 ^1A_g $\pi \rightarrow \pi^*$	5.86	4.76	5.80	92	6.14	
2 ^1B_g $n \rightarrow \pi^*$	6.07	3.82	5.64	94	6.40	
1 ^1A_u $\sigma \rightarrow \sigma^*$	6.13(0.00)	3.88(0.00)	5.78(0.00)	90	6.49	
2 ^1A_u $\sigma \rightarrow \sigma^*$	6.24(0.00)	4.22(0.00)	5.97(0.00)	91	6.57	

[a] Calculated CC2/aug-cc-pVTZ vertical excitation energies (in eV) in comparison to CCSD,[5] SOPPA,[4] TDDFT/BP86, and experimental data. For dipole-allowed transitions the oscillator strengths (calculated in the length gauge) are given in parentheses. [b] Reference 52, recorded in gas phase. [c] Reference 50, recorded in ethanol. [d] Reference 51, recorded in ethanol. The oscillator strengths are 0.56 for 1 ^1B_u and 0.24 for 3 ^1B_u.

Table 6. UV Spectrum of *cis*-Azobenzene[a]

	SOPPA,[4]	TDDFT	CC2			CCSD	
	[3s2p(1c)/2s]	aug-TZVP	aug-cc-pVTZ	%T1	$\Delta\mu$	extrapolated	expt
1 ^1B $n \rightarrow \pi^*$	2.52(0.01)	2.34(0.05)	3.00(0.03)	94	0.61	3.17	2.92,[b] 2.8,[c] 2.87[d]
2 ^1B $\pi \rightarrow \pi^*$	4.30(0.03)	3.44(0.02)	4.49(0.06)	91	1.95	4.67	4.4,[c] 4.42[d]
2 ^1A $\pi \rightarrow \pi^*$	4.51(0.02)	3.55(0.00)	4.65(0.02)	92	2.26	4.83	
3 ^1B $\pi \rightarrow \pi^*$	4.66(0.09)	3.57(0.01)	4.79(0.07)	92	1.15	5.09	4.68[b,e]
3 ^1A $\pi \rightarrow \pi^*$		3.68(0.00)	4.82(0.00)	91	0.21	5.02	

[a] Calculated CC2/aug-cc-pVTZ vertical excitation energies (in eV) in comparison to CCSD, SOPPA,[4] DFT-BP86, and experimental data.[53] The oscillator strengths are given in parentheses for the length representation. $\Delta\mu$ is the difference of the dipole moment between the ground state and the excited state (in debye). [b] Reference 52, recorded in gas phase. [c] Reference 50, recorded in ethanol. [d] Reference 51, recorded in ethanol; a third band was observed at 5.10 eV, but the assignment of this band is unclear. The oscillator strengths are 0.22 for 1 ^1B and 0.17 for 2 ^1B. [e] Assignment unclear; the observed band covers probably 2 ^1A and 3 ^1B.

C—N stretching mode, which gives rise to one of the most intensive bands (11 b_u) at 1295−1300 cm^{-1},[47,48] and its symmetric counterpart (11 a_g) which is observed at 1218−1225 cm^{-1}.[46−48] In the MP2/cc-pVTZ spectrum, these modes are found at 1265 and 1211 cm^{-1}, respectively, while the DFT-BP86 results are 1218 and 1175 cm^{-1}. These three bands ($\nu_{N=N}$, symmetric and asymmetric ν_{C-N}) and the mode 12 a_g, which also has some contribution from $\nu_{N=N}$, are the only vibrations in the region 1000−1500 cm^{-1} where the MP2/cc-pVTZ harmonic frequencies are more than a few cm^{-1} below the experimental fundamental bands. For most of the bands, the MP2 results are about 20 cm^{-1} above the experimental values, as it is expected for a comparison of calculated harmonic frequencies with fundamental bands. The DFT-BP86 results show the usual tendency to underestimate the harmonic frequencies.

As expected for this kind of molecules, MP2 describes the vibrational spectrum consistently more accurate than DFT, which, however, requires much less computational effort. Typically, the deviations between the MP2 harmonic frequencies and the experimental results are about half of the deviations found for DFT. An exception is, however, the ν_{C-H} stretching modes, for which anharmonic effects are large, as can be concluded from results for benzene.[45] Since we have not considered aharmonicities, one cannot expect a very close description of all experimental bands. Nevertheless, the present harmonic MP2/cc-pVTZ frequencies lead to a comparatively good agreement.

4.2. Vibrational Spectrum of *cis*-Azobenzene. The vibrational spectrum of *cis*-azobenzene is difficult to assign since fewer experimental data are available. We find, however, mostly the same trends as those for the trans isomer. For the region up to 1000 cm^{-1}, the MP2 and DFT-BP86 spectra agree well with the experiment. In particular, the MP2 results are for all bands within 20 cm^{-1} of the experimental results. Above 1000 cm^{-1}, the deviations become slightly larger and the assignment is less certain. Nevertheless, the agreement is quite satisfactory for most observed frequencies apart from two bands observed at 1575 and 1585 cm^{-1},[48] which are difficult to assign to any of the harmonic frequencies.

The N═N stretching frequency is found at 1469 cm^{-1} (MP2) and 1504 cm^{-1} (DFT). As for the trans isomer, this mode has the largest ^{15}N isotopical shift. In the experimental spectrum, the N═N stretching mode is assigned to the band at 1511 cm^{-1}. The C−N stretching modes are obtained at 1102 and 1153 cm^{-1} in the DFT-BP86 spectrum and at 1166 and 1177 cm^{-1} in the MP2 spectrum. The experimental assignment of these modes is uncertain, but most likely they have to be assigned to the bands observed at 1093 and 1152 cm^{-1}. For most bands, the MP2 frequencies are above the experimental values, as expected for a comparison of harmonic frequencies with fundamental bands, while the DFT-BP86 frequencies are below the experimental results. On the average, MP2 gives a somewhat better agreement with experiment than DFT, which is, however, computationally much less demanding.

5. UV Spectra of *trans*- and *cis*-Azobenzene

The lowest vertical singlet excitation energies of *trans*- and *cis*-azobenzene were calculated at the CC2/aug-cc-pVTZ and the DFT-BP86/aug-TZVP level. The results are listed in Tables 5 and 6 in comparison with available experimental data and the results from SOPPA calculations.[4] For the dipole-allowed transitions, the oscillator strengths are given in parentheses.

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These values were obtained in the length representation of the dipole operator; velocity and mixed representations lead to similar results. Note that the experimental results refer to band maxima in absorption spectra, while ab initio results are for vertical electronic excitations, which limits the comparability. For CC2, also the percentage contribution of single excitations (%T1) is given. This value should be between ~90 and 100%; otherwise CC2 gives less reliable results.

5.1. Electronic Spectra of *trans*-Azobenzene. The most prominent feature in the experimental absorption spectum of *trans*-azobenzene is constituted by the $\pi\pi^*$ excitation into the S_2 state ($1\ ^1B_u$). The calculated results for this transition are 4.04 eV (CC2), 3.90 eV (SOPPA), and 3.29 eV (DFT). All three methods give for this excitation the largest oscillator strength. Since the experimental results from refs 50 and 51 were recorded in ethanol as solvent, they are only comparable up to a certain degree with the theoretical results, which refer to the gas phase. The only available experimental gas-phase results are those from ref 52. The latter agrees for all three observed states very well with the CC2 values, with a deviation of only 0.02, 0.08, and 0.15 eV for $1\ ^1B_g$, $1\ ^1B_u$, and $3\ ^1B_u$, respectively. This agreement is somewhat fortunate since the average error of CC2 vertical excitation energies is usually larger than 0.1 eV. This accuracy is first obtained at the CCSD or a higher level of the CC hierarchy. With accurate basis sets, such calculations are prohibitive for molecules as large as azobenzene. We can, however, estimate the correction of higher-order correlation contributions from the difference between the CC2 and CCSD values calculated in a smaller basis set. When adding the difference between the CC2 and CCSD vertical excitation energies calculated in the [3s2p1d/2s] ANO basis to the CC2/aug-cc-pVTZ values, one obtains the "CCSD/extrapolated" results[5] listed in Table 5. For S_1, the correction is negligible, but, for the S_2 and $3\ ^1B_u$ states, the CCSD results are ~0.3 eV higher and are, as expected for a comparison of vertical excitation energies with band maxima, slightly blue shifted compared to the experimental values.

For SOPPA and, even more, for DFT-BP86, the deviations are considerably larger. While the SOPPA results for $1\ ^1B_u$ and $3\ ^1B_u$ are in acceptable agreement with the experiment ($\approx$ 0.2 eV devivation), the excitation energy for the S_1 state ($1\ ^1B_g$) is too low by ~0.3 eV and the DFT-BP86 results are red shifted for all states between 0.6 ($1\ ^1B_g$) and 1.8 eV ($2\ ^1B_g$). In addition, we tried the B3LYP hybrid functional (aug-cc-pVTZ basis and the BP86/aug-cc-pVTZ geometry), but this calculation also gave considerably red shifted results (~0.3−0.4 eV compared to the experimental values).

Thus, from the methods which can be applied to calculate excitation energies to molecules of this size, CC2 gives the most accurate results. The excitation energies obtained from DFT are for all states distinctly more red shifted compared to the experimental band maxima than the CC2 and SOPPA values and, thus, are less appropriate for this class of molecules.

5.2. Electronic Spectra of *cis*-Azobenzene. The investigation of the UV spectrum of the cis isomer leads to similar conclusions. For *cis*-azobenzene, we calculated at the CC2/aug-cc-pVTZ level also the change of the dipole moment upon excitation ($\Delta\mu$), which provides a measure for the charge-transfer character of the transition. The $\pi\pi^*$ transition ($2\ ^1B$) is found in the CC2 calculation at 4.49 eV and the $n\pi^*$ transition ($1\ ^1B$) at 3.00 eV, while the SOPPA values are 4.30 and 2.52 eV and the DFT-BP86 results are 3.37 and 2.33 eV, respectively. The differences between the dipole moments of the ground state and the excited state clearly show the charge-transfer character for the $2\ ^1B$ state. The CC2/aug-cc-pVTZ result for the S_1 state of 3.00 eV agrees, as for the trans isomer, very well with the experimental gas-phase result from ref 52 of 2.92 eV. Again, DFT-BP86 gives rather unsatisfactory results, strongly red shifted compared to the experimental values.

6. Summary

The geometries of *trans*- and *cis*-azobenzene were optimized at the MP2/cc-pVTZ level and compared with the available experimental data[37−39] and DFT-BP86 results. Our calculations confirm the planar C_{2h}-symmetric structure, which was found in a recent gas electron diffraction experiment[37] for *trans*-azobenzene. Both quantum chemical methods reproduce the experimental results within the expected accuracy. For *trans*-azobenzene, BP86/TZVP and MP2/cc-pVTZ give very similar structures, in particular almost the same N═N bond length, while B3LYP/cc-pVTZ gives a 2 pm shorter result for the N═N bond length. For *cis*-azobenzene, all three methods are in close agreement for the N═N bond length. The MP2/cc-pVTZ optimized geometries are the most accurate ab initio r_e structures available for the azobenzenes. These structures should allow for a refined analysis of the GED experiments which are presently based on less accurate DFT calculations.

For both, *trans*- and *cis*-azobenzene and their ^{15}N isotopomers harmonic frequencies were evaluated at the MP2/cc-pVTZ and the DFT-BP86/TZVP levels and compared with the experimental results from various studies.[46−49] In comparison to the experiment, the MP2 frequencies tend to be blue shifted, while the DFT results show a tendency for a red shift. These deviations are most likely caused by the harmonic approximation. Furthermore, the DFT method shows in this case a systematic underestimation of the force constants.

The vertical excitation energies and oscillator strengths for the lowest singlet states were calculated by CC2/aug-cc-pVTZ and DFT-BP86/aug-TZVP. For the S_1 and S_2 state in *trans*-azobenzene and the S_1 state in *cis*-azobenzene, we find a fortuitous agreement between the CC2 results and experimental results from gas-phase spectra. Because of the charge-transfer character of these states, DFT-BP86 gives strongly red shifted vertical excitation energies which exhibit large errors between 0.6 and 1.8 eV. The red shifts are somewhat smaller with the B3LYP functional, but the results remain unsatisfactory.

Since MP2 and CC2 are, in connection with the resolution-of-the-identity approximation, applicable to systems with 20 and more non-hydrogen atoms, the combination of MP2 geometry optimizations and CC2 calculations for the electronic spectra turns out as the method of choice for the investigation of substituent effects on the structure and the optical properties of azobenzenes. DFT methods are found to be less appropriate, while more accurate coupled-cluster methods, as for example CCSD, are today too expensive for molecules of this size.

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Acknowledgment. This work was supported by the Center for Functional Nanostructures (CFN) of the Deutsche Forschungsgemeinschaft (DFG) within project C2.

Supporting Information Available: Table of IR spectrum data of *trans*-azobenzene and table of calculated DFT/TZVP and MP2/cc-pVTZ harmonic frequencies of *cis*-azobenzene in comparison with experimental fundamental bands. This material is available free of charge via the Internet at http://pubs.acs.org.

JA034433O