

Ab Initio Study on the Excitation Energies of the Protonated Schiff Base of 11-*cis*-Retinal

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Ab initio computational results from MRSD-CI with split-valence basis set plus d orbitals predict that the first excited of the protonated Schiff base of retinal (PSBR) is the ionic, strongly allowed, 1B_u state. Our best estimate for the excitation energy of this state of the isolated PSBR cation is 2.7 ± 0.5 eV, in agreement with the solution spectra. The higher singlet excited states of PSBR were found to be mixed in bonding character, and only a vague line can be drawn between the ionic and covalent states. In contrast to the conventional assignment of the spectra of PSBR, which assumes the second excited state to be covalent 1A_g , this state was found to be mostly ionic. It is the third excited state that has a wave function closer to that of the covalent 1A_g state, although the two-electron excitation from π_6 to π_7^* only makes a small contribution to its wave function. The fourth excited state calculated was also a covalent state and 1A_g -like. The wave functions of the two ionic excited states computed are essentially monoconfigurational, and those of the two covalent excited states are both multiconfigurational. The ground-state charge density concentrates on the N₁₆, C₁₅, C₁₃, and C₁₁ atoms. It is found that there is a large decrease of bond alternation from the ground state to the 1B_u state. The overall overlap population becomes smaller and smaller for the higher excited states. Comparison of the excited states of PSBR and dodecahexaene at the π SDTQSC-CI/STO-3G level proves that the nature of the excited states of PSBR is very different from that of dodecahexaene in this approximation.

The photoexcitation of the protonated Schiff base of retinal (PSBR) is the primary event of vision¹ and the first step in mechanism of the proton translocation in bacteriorhodopsin.² The excited state of PSBR in rhodospin resulting from light absorption undergoes geometric isomerization prior to the subsequent biological processes.^{3,4} The chemical structure PSBR is 11-*cis* in rhodospin, as shown schematically in Figure 1, and all-*trans* in bacteriorhodopsin. In rhodospin, PSBR is believed to be connected with the protein backbone through a covalent bond between the nitrogen atom and lysine. Hydrogen bonding could be formed with a negative counterion such as the carboxylate anions, which has a strong effect in regulating the maximum absorption of rhodopsin.^{5,6} Point charges surrounding PSBR also effectively regulate the maximal absorption wavelength of rhodopsin.⁷ One objective of this presentation is to examine the charge distribution of the isolated PSBR cation at its ground-state 11-*cis* geometry and the changes of charge density and bond orders after vertical excitations.

There are two low-lying excited states of PSBR that are presumed to be of primary interest, the ionic 1B_u -like state and the covalent 1A_g -like state. For medium- and long-chain polyenes in condensed phase, it has been shown that the 1A_g -like state is lower in energy.⁸ Both 11-*cis*-retinal⁹ and its Schiff base¹⁰⁻¹² have a similar order of the excited-state energies to that of polyenes. Protonation of the Schiff base stabilizes the ionic state selectively and reverses the energy order. Recent experiments applying two-photon spectroscopy reported that the lowest excited state of locked 11-*cis*-PSBR in a sodium phosphate buffered solution is the 1B_u -like state at 2.6 eV and that the next excited state is

TABLE I: Major Geometric Parameters of PSBR Optimized with MMX (For Atom Numbering See Figure 1)

R X	H H	<i>n</i> -C ₄ H ₉ H	<i>n</i> -C ₄ H ₉ H...C ₃ H ₇ CO ₂ ⁻
Bond Lengths, Å			
R6-5	1.354	1.358	1.354
R7-6	1.493	1.480	1.490
R8-7	1.354	1.362	1.355
R9-8	1.475	1.460	1.472
R10-9	1.366	1.386	1.370
R11-10	1.465	1.433	1.457
R12-11	1.360	1.390	1.368
R13-12	1.476	1.428	1.459
R14-13	1.363	1.412	1.382
R15-14	1.464	1.407	1.438
R16-15	1.283	1.363	1.344
Bond Angles, deg			
A7-6-5	120.6	121.4	121.2
A8-7-6	122.4	122.6	122.6
A9-8-7	125.3	125.3	124.7
A10-9-8	118.1	118.0	118.4
A11-10-9	124.9	125.0	124.6
A12-11-10	126.6	127.0	127.5
A13-12-11	128.7	129.8	129.8
A14-13-12	117.6	117.3	117.3
A15-14-13	125.3	125.7	125.4
A16-15-14	120.2	121.7	121.3
Dihedral Angles, deg			
B8-7-6-5	57.9	57.1	57.1
B9-8-7-6	-178.6	179.8	178.4
B10-9-8-7	-165.8	-170.3	167.8
B11-10-9-8	179.0	176.0	-175.9
B12-11-10-9	-172.5	-178.6	-169.0
B13-12-11-10	10.3	18.0	12.2
B14-13-12-11	-153.5	-164.3	-165.2
B15-14-13-12	-179.9	177.2	-179.7
B16-15-14-13	177.8	179.8	173.0

the 1A_g -like state at 2.8 eV.^{13,14}

Although the 1B_u state, being the first excited state, is primarily responsible for the light absorption of rhodopsin, the 1A_g state is believed to be important in the geometric isomerization from 11-*cis* to 11-*trans* structure. It has been shown^{15,16} that, as the C₁₁-C₁₂

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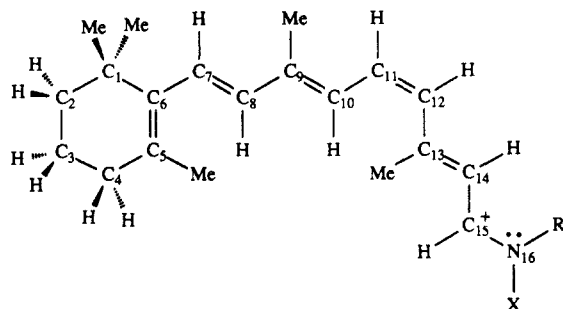


Figure 1. Atom numbering of 11-*cis*-PSBR. R = H, *n*-C₄H₉; X = H, H₂C=CHCO₂⁻. Energy calculations were performed with R = X = H.

bond twists, the mixing of the ¹A_g state into the ¹B_u state becomes more and more intense. For *all-trans*-retinal Schiff base, the ¹B_u state is only lower than the ¹A_g state in energy.¹⁴ Another objective of this study is to predict the energies of ¹B_u, ¹A_g, and other higher excited states of 11-*cis*-PSBR at its ground-state geometry.

Salem and Buckmann have applied ab initio methods in the study of charge separations of PSBR upon geometry distortion induced by light absorption.¹⁷ Their diradical model provided an elegant sudden polarization mechanism of the excited singlet state initiating an electric signal leading to vision. It was found, however, that this model was oversimplified and that deprotonation of PSBR is essential for the initiation of visual transduction.¹⁸ A few ab initio calculations on the ground-state charge density and bond orders of PSBR also appeared subsequently in the literature.¹⁹⁻²¹ A more quantitative study of the excitation energy and detailed analysis on the charge densities and overlap populations through ab initio method, however, are needed.

Geometries and Basis Set

Although in solution 11-*cis*-retinal is populated with both 12-*s-cis* and 12-*s-trans* conformations,^{22,23} only the 12-*s-trans* geometry was adopted in this study. Geometry optimizations were carried out with the MMX empirical force field method of the PCMODEL programs.²⁴ Table I lists the major geometric parameters optimized for PSBR with three different sets of nitrogen substituents R and X. To accommodate the bulky ionone ring and the methyl groups, there is some twisting of the single bonds out of conjugation. For free PSBR (R = X = H), the optimized geometry has a 57.9° twisting from the 0° of the *s-cis* conformation around the C₆-C₇ bond and 26.5° twisting from the 180° of the *s-trans* conformation around the C₁₂-C₁₃ bond. There is also a smaller 14.2° twisting along the C₈-C₉ bond. Most double bonds, however, remain planar. On exception is the C₁₁=C₁₂ bond, which is twisted by 10.3° from *cis* conformation.

Replacing one hydrogen of the NH₂ group by a butyl group (R = *n*-C₄H₉, X = H) decreases bond alternation of the single and double bonds. This effect is the largest for the bonds near N₁₆ and becomes smaller toward the C₅ end of the chain. The effect of alkylation on bond angles and dihedral angles is small, except for the twisting around C₁₁=C₁₂ which is increased by 7.7° and around C₁₂-C₁₃ which is decreased by 10.8°. The addition of a butoxyate counterion (R = *n*-C₄H₉, X = H₂C=CHCO₂⁻) next to the NH group draws the positive charge density distributed along the polyene chain toward the N₁₆ atom. As a result of this charge localization on nitrogen, bond alternation is increased. The

dihedral angle along C₇-C₈-C₉-C₁₀ changes from -170.3° to 167.8°. There is very little change in other bond angle and dihedral angles caused by the hydrogen bonding.

RHFSCF and CI calculations were performed on the unsubstituted PSBR with the MELDF package of programs.²⁵ To limit the total number of atoms, the saturated carbon atoms attached to the conjugation system were replaced with hydrogen atoms with the C-H bond length being 1.08 Å, keeping all other geometrical parameters fixed at the MMX structure. A Dunning-Hay split-valence basis set²⁶ was included for all atoms, with a set of five-component d orbitals augmented on the 12 C and N atoms. Since the low-lying excited states did not involve Rydberg states as found in the previous study on the short-chain homologues of PSBR,²⁷ Rydberg orbitals were not introduced into the basis set. The resulting total number of basis functions is 196.

Excitation Energies

For the ground state of PSBR, the RHFSCF calculation was performed. Figure 2 shows the contour plots of the six occupied π orbitals of the ground state. Mostly localized on the C=N double bond, π_1 (a₃₀) is lower than several σ orbitals in energy because of the lower atomic orbital energy of the contributing N 2p_z. The orbital π_2 is lower than one bonding σ orbital in energy. Orbitals π_3 to π_6 correspond to the four highest occupied orbitals. Since the geometry of PSBR does not have a plane of symmetry, there is mixing between the π and the σ orbitals. (These orbitals should therefore be called " π -like" orbitals.) This mixing is especially intense between π_2 (a₃₈) and the nearby σ orbitals a₃₇ and a₃₉, which are not shown in Figure 2. With the increasing number of nodes, the nodal patterns are clearly recognizable for all the π orbitals.

The RHFSCF wave function was also converged for the ³B_u-like state with orbitals π_6 and π_7 singly occupied. Figure 3 shows the molecular orbital energy diagram of the ground state and the ³B_u state. All occupied π orbitals and some virtual orbitals that are important for the dominant configurations of the excited states are included in the figure. From the ground state to the ³B_u state, the π_1 orbital is lifted in energy, while the energies of π_2 to π_6 have little change.

To increase the speed of convergence for the CI calculations and to provide a better set of molecular orbitals in describing the excited states with the CI wave functions, the virtual orbitals of the ground state were transformed to the K orbitals of Feller and Davidson.²⁸ During the integral transformation, only a portion of the molecular orbital space was transformed, for the following limited CI only allows electron excitations to take place within this portion. The first 24 orbitals are composed of 1s carbon and nitrogen atomic orbitals and 12 MO's that are mostly 2s atomic orbitals. These MO's were treated as core orbitals during the integral transformation. The highest 60 virtual orbitals, which are composed mostly of d functions, were truncated. As a result, 112 active orbitals were left, which represent a conceptual split-valence space.

To obtain a reference space for the multiconfigurational single and double CI calculations of the excited-state energies, 10 roots were sought from a preliminary CI calculation, in which severe limitations of electron excitations were applied. In this preliminary CI, single excitations were allowed from the occupied orbitals a₂₅ to a₄₃ into the conceptual minimal space limit a₄₄ to a₇₄, starting from the Hartree-Fock configuration of the ground state. Double excitations into an arbitrary smaller set of virtual orbitals a₄₄ to a₅₉ were also permitted.

MRSD-CI(I) was subsequently performed for the first five roots. In the reference space, 18 configurations with coefficient

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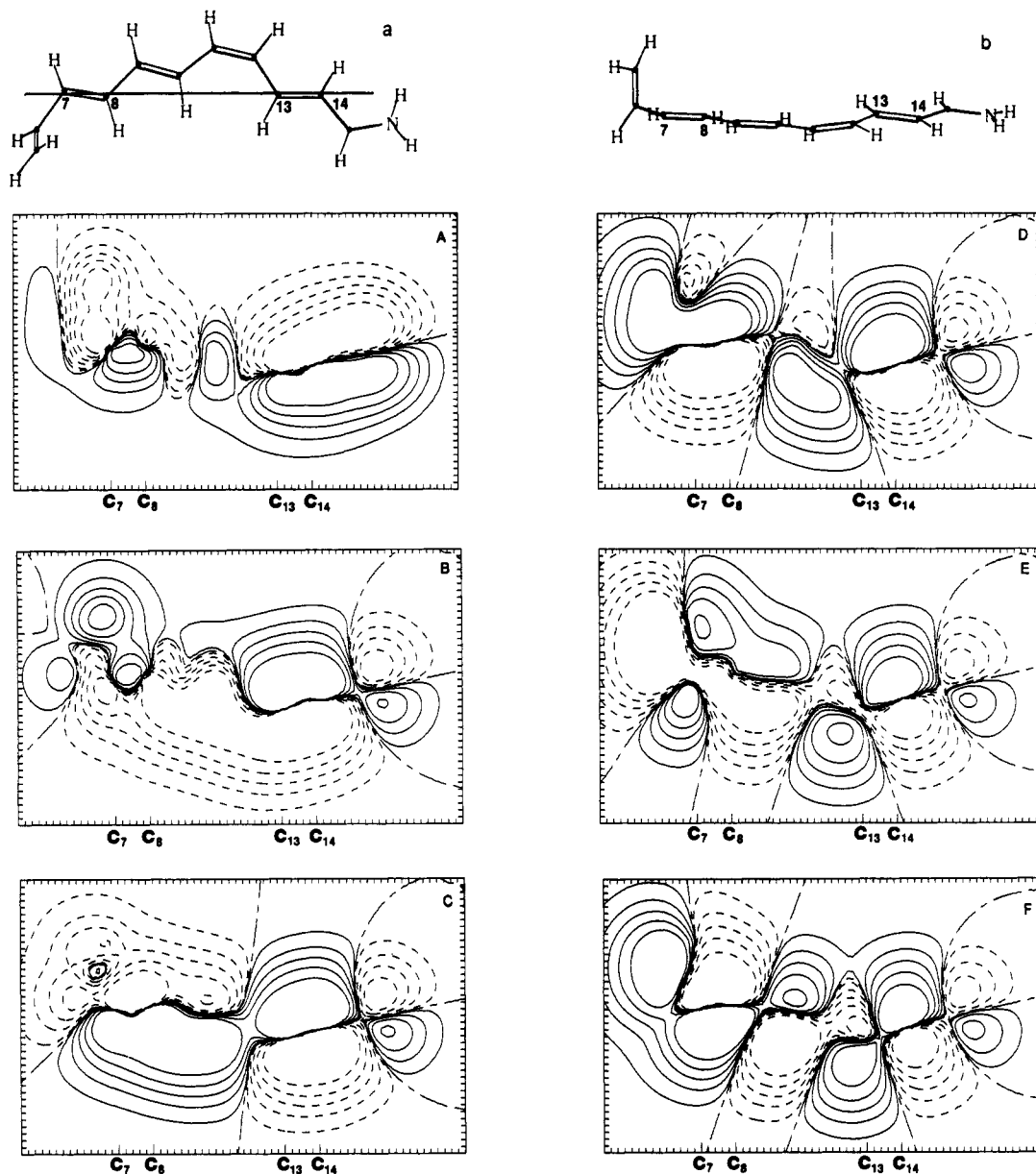


Figure 2. π MO's of ground-state PSBR. As shown in inset a, the plotting plane cuts through roughly $C_7=C_8$ and $C_{13}=C_{14}$. Inset b shows what the molecular skeleton looks like in the plotting plane. Because the PSBR molecule is not planar (only nearly so for the two fragments, C_7 to C_{12} and C_{13} to N_{16}), this plane is only approximately perpendicular to the nodal plane of the π system that extends from C_7 to N_{16} . (A) Ground-state MO, π_1 ; (B) ground-state MO, π_2 ; (C) ground-state MO, π_3 ; (D) ground-state MO, π_4 ; (E) ground-state MO, π_5 ; (F) ground-state MO, π_6 .

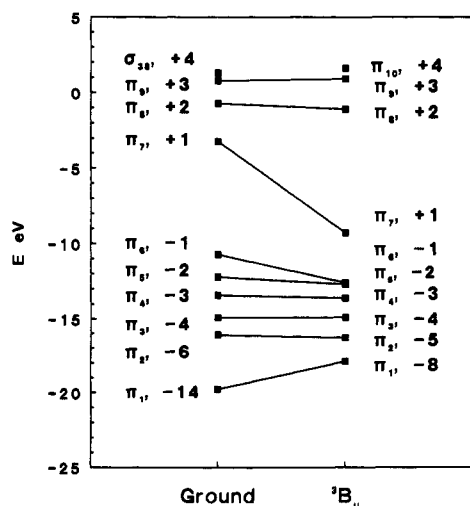


Figure 3. Energy diagram for the occupied π orbitals and some virtual orbitals of the ground state and the 3B_u state of PSBR.

contribution 0.1 or larger were included. Single and double excitations were allowed from the occupied orbitals a_{25} through a_{39} . Excitations up to quadruples were allowed within the reference space, which is in the range of a_{40} to a_{47} . Single and double excitations were allowed to the conceptual minimal space limit a_{48} to a_{74} , and additional single excitations were allowed to the split-valence space limit a_{75} to a_{136} . Second-order Rayleigh-Schroedinger perturbation theory²⁹ was applied to select the most important configurations from each root to be included in the variational CI. Only about half of the available correlation energy of each state was included in the 158 021 configurations selected. The full correlation energies available from the MRSD-CI were then extrapolated by perturbation theory and corrected to the quadruple excitation level with the Davidson formula.³⁰⁻³³

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TABLE II: Relative Energies and Dominant Configurations of the First Five States of PSBR Calculated from the MRSD-CI(I)^a with the Ground-State Orbitals

state	<i>f</i>	ΔE_{ref}^b	$\Delta E_{\text{trunc}}^c$	ΔE_{SDQ}^d	dom confign	coeff ^e
1 1^1A_g		0.0 ^f	0.0 ^g	0.0 ^h	HF	0.9253
2 1^1B_u	2.59	7.2	7.1	3.8	(-1,+1)	0.8226
					(-1,+2)	0.3092
					(-1,+3)	0.1844
3 2^1A_g	0.33	8.9	8.9	5.4	(-2,+1)	0.8720
4 3^1A_g	0.13	9.4	10.3	5.2	(-1,+2)	0.5565
					(-3,+1)	0.4914
					(-1,+1)	0.3049
					(-1,+3)	0.2558
					(-1,+1) ²	0.1667
5 4^1A_g	0.31	10.3	10.7	5.4	(-3,+1)	0.6587
					(-1,+2)	0.3885
					(-1,+1)	0.2337
					(-1,+4)	0.2038
					(-3,+2)	0.1915
					(-1,+3)	0.1801

^aGround state canonical and K orbitals were used. The reference space includes 18 configurations. Excitations from the 1s and 2s orbitals were not allowed. Double excitations were allowed through minimal space. Single excitations were allowed through the SV space. ^bZero-order energy from the reference space. ^cVariational CI energy with truncation of second-order Rayleigh-Schrodinger perturbation theory. ^dPerturbation extrapolated CI energy plus the Davidson correction for the correction of quadruple excitations. For extrapolation formula, see ref 32. ^eConfigurations with coefficients larger than 0.16. ^f-478.899 51 hartrees. ^g-479.208 22 hartrees. ^h-479.542 60 hartrees.

As expected, the second state of PSBR was found to be the singly excited state 1^1B_u (Table II). The only dominant configuration of 1^1B_u is (-1,+1), resulting from the excitation of one electron from the first orbital below the Fermi surface to the one above it. The extrapolated excitation energy for this state (3.8 eV), however, is too high compared to the experimental values. This is because the 1^1B_u state is highly polarized and can only be poorly described by the limited CI wave function based on the ground-state orbitals. Lack of diffuse functions in the basis set is another source of error in the high excitation energy calculated for 1^1B_u . As shown in Table II, the 1^1B_u -state transition was found to be highly allowed and to have an oscillator strength of 2.59.

The spacing between the energies of the third through the fifth states are calculated to be smaller. The third state also has only one dominant configuration in its wave function, but it is (-2,+1). Being monoconfigurational, this state is likely to be an ionic 2^1A_g state. The fourth and the fifth states are both multiconfigurational states with different linear combinations of the same group of dominant configurations (-1,+2), (-3,+1), and (-1,+1). These states are labeled as 3^1A_g and 4^1A_g . The assignments of these states as 1^1A_g -like are based on the fact the (-1,+2) excitation for polyene gives 1^1A_g symmetry. The small oscillator strengths for these states (0.33, 0.13, and 0.31) suggest that the assignment of 1^1A_g is a close approximation. It should be noted, however, that there are ambiguities in these assignments because of the lack of symmetry.

As one goes from the ground state to the fifth state, the state energies obtained from the reference space and the truncated CI increase (Table II). After the extrapolation of the correlation energy and the correction of the quadruple excitations, the energies of 2^1A_g and 3^1A_g are reversed, indicating that the extrapolation is not reliable. As a result, it is not clear what is the energy order of these states based on the results of MRSD-CI(I). A better CI calculation, therefore, is needed.

From the MRSD-CI(I) wave functions, average natural orbitals (ANO) were calculated for the ground state and the four excited states. Among these ANO's, the virtual orbitals up to a_{110} have relatively large occupation numbers (larger than 0.0001). In the subsequent CI calculation, MRSD-CI(II), single and double excitations were allowed up to orbital a_{110} and no excitations were allowed to the higher virtual orbitals. The reference space included 15 configurations with coefficient contribution of each larger than

TABLE III: Relative Energies and Dominant Configurations of the First Five States of PSBR Calculated from the MRSD-CI(II)^a with the Average Natural Orbitals Calculated from the CI Wave Functions of MRSD-CI(I)

state	ΔE_{ref}^b	$\Delta E_{\text{trunc}}^c$	ΔE_{SDQ}^d	dom confign	coeff ^e
1 1^1A_g	0.0 ^f	0.0 ^g	0.0 ^h	HF	0.9214
2 1^1B_u	5.5	6.3	3.7	(-1,+1)	0.8351
				(-1,+2)	0.3485
3 2^1A_g	7.5	8.1	5.3	(-2,+1)	0.8826
4 3^1A_g	7.8	9.5	6.0	(-3,+1)	0.6884
				(-1,+2)	0.4558
				(-1,+1) ²	0.2331
5 4^1A_g	9.1	10.0	6.2	(-1,+2)	0.6567
				(-3,+1)	0.5127
				(-1,+1)	0.2919

^aThe reference space includes the 15 most important configurations (with coefficient $c_i > 0.05$). Excitations from the 1s and 2s orbitals were not allowed. Single and double excitations were allowed through orbital a_{110} , which has ANO occupation numbers larger than 0.0001. ^bZero-order energy from the reference space. ^cVariational CI energy with truncation of second-order Rayleigh-Schrodinger perturbation theory. ^dPerturbation extrapolated CI energy plus the Davidson correction for the correction of quadruple excitations. For extrapolation formula, see ref 32. ^eConfigurations with coefficients larger than 0.20. ^f-478.897 43 hartrees. ^g-479.249 24 hartrees. ^h-479.574 34 hartrees.

0.05. Perturbation selection reduced the number of spin-adapted configurations to 163 312, which accounted for more than 60% of the available correlation energy for the ground state and about 50% for the excited states.

The effect of expanding the CI wave functions over ANO on the energies of the five states is very different. By inspecting Tables II and III, one finds that the extrapolated total energy of the ground state calculated from MRSD-CI(II) is 0.9 eV lower than the energy from MRSD-CI(I), an improvement resulting from the better description of the excited configurations by the ANO. There are similar stabilizations for the second and the third states, resulting in small changes in excitation energies for these two states.

From the list of the dominant configurations of the fourth and the fifth states, one can see that the first two configurations are reversed for both states in comparison to the results of MRSD-CI(I) and MRSD-CI(II). The stabilizations of these two states introduced by the usage of ANO are smaller compared to the first three states. As a result, there is an increase of the excitation energy from 5.2 to 6.0 eV for the fourth state and from 5.4 to 6.2 eV for the fifth state. This inconsistency indicates that the excitation energies predicted for the fourth and fifth states are less accurate.

Substantial improvement on the excitation energy of the 1^1B_u state was sought by computing MRSD-CI with two different sets of orbitals. To obtain the ground-state energy, the ANO's from the MRSD-CI(I) were used. All configurations of the first and the second roots with coefficient contribution larger than 0.05 were selected to form the reference space. The same type of electron excitations as in MRSD-CI(II) was allowed from this configuration set. Perturbation truncations kept 143 200 spin-adapted configurations and included 70% of the correlation energy available in the variational CI. The footnotes of Table IV contain the results for the ground state.

To obtain the 1^1B_u state energy, the 3^1B_u K orbitals were used in the MRSD-CI calculation. Eight configurations with coefficient contributions larger than 0.08 were included in the reference space. The same excitations as those in MRSD-CI(I) were allowed from this reference space. Perturbation truncation kept 145 303 spin-adapted configurations and accounted for 51% of the correlation energy available. The CI results for the 1^1B_u excitation energy before and after extrapolation are listed in Table IV. The excitation energy of the 1^1B_u state estimated after extrapolation is 2.7 ± 0.5 eV, which is our best estimate of this quantity. As in the other CI wave functions of 1^1B_u , in this CI wave function there is also a large mixing of the (-2,+1) configuration (with

TABLE IV: Excitation Energy of the 1B_u State Calculated with ANO for the Ground-State MRSD-CI^a and the 3B_u Orbitals for the 1B_u MRSD-CI^b

state	ΔE_{ref}^c	ΔE_{trunc}^d	ΔE_{SDQ}^e
ground	0.0 ^f	0.0 ^g	0.0 ^h
1B_u	3.6	6.1	2.7

^a Average natural orbitals for the five states in Table II were used. The reference space included 11 configurations with coefficients larger than 0.05 for both ground and 1B_u states. The same type of excitations as those described in MRSD-CI(II) was allowed. ^b The 3B_u orbitals were used. The reference space included eight configurations with coefficient contribution larger than 0.08 for both ground and 1B_u states. The same type of excitations as in MRSD-CI(I) was allowed. ^c Zero-order energy from the reference space. ^d Variational CI energy with truncation of second-order Rayleigh-Schrodinger perturbation theory. ^e Perturbation extrapolated CI energy plus the Davidson correction for the correction of quadruple excitations. For extrapolation formula, see ref 32. ^f -478.893 92 hartrees. ^g -479.282 56 hartrees. ^h -479.567 35 hartrees.

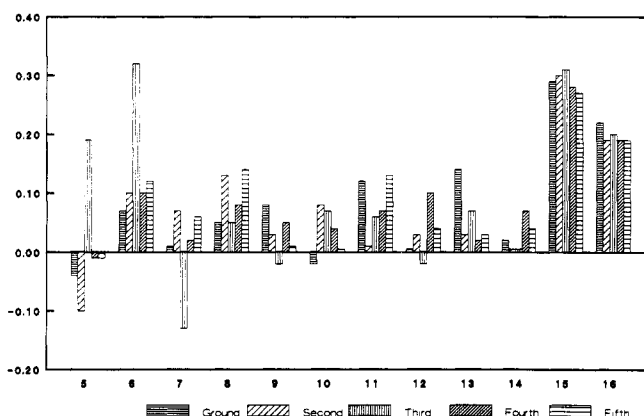


Figure 4. Charge distributions of the ground state and the excited states of PSBR with the MRSD-CI(I) wave functions from Mulliken population. Hydrogens are combined to the neighboring carbon or nitrogen atoms.

coefficient 0.3034) with the $(-1,+1)$ configuration (with coefficient 0.8357). Unfortunately, a similar calculation was not possible for the higher excited state because we were unable to obtain a corresponding excited-state SCF wave function.

Population Analyses

Mulliken population analyses for the ground state and the four excited states of PSBR were performed with the MRSD-CI(I) wave functions. The positive charges are almost always distributed among the hydrogen atoms, which are less electronegative than carbon and nitrogen. For the ground state, in fact, the only carbon atom that is positively charged is C_{15} . The nitrogen atom is actually negatively charged.

The "group charge", obtained by adding the charge of the carbon or nitrogen atom and the charges of the neighboring hydrogen atoms, may have more chemical significance. For the ground state, this group charge shows a simple pattern (Figure 4). While the NH_2 group bears a large positive charge (0.22), the largest positive charge is on the adjacent CH group (0.29). This suggests that the two major resonance structures, $-CH^+-NH_2$ and $-CH=NH_2^+$, are both important in the wave function of the ground state of PSBR. With a decreasing magnitude, positive charges are found on the alternate carbon atoms along the chain, corresponding to the other less important resonance structures, $-CH^+-CH=CH-NH_2$, etc. From C_{15} to C_{13} , C_{11} , and C_9 , the positive charge decreases from 0.29 to 0.14, 0.12, and 0.08, respectively. The other set of alternate carbons and the chain terminal further away from the nitrogen remain essentially neutral. Overlap populations of the C-N bond and the adjacent C-C bond are quite similar for the ground state (Figure 5). In contrast to the decrease of the positive charge on going from the nitrogen atom toward the other end of the chain, the bond alternation increases.

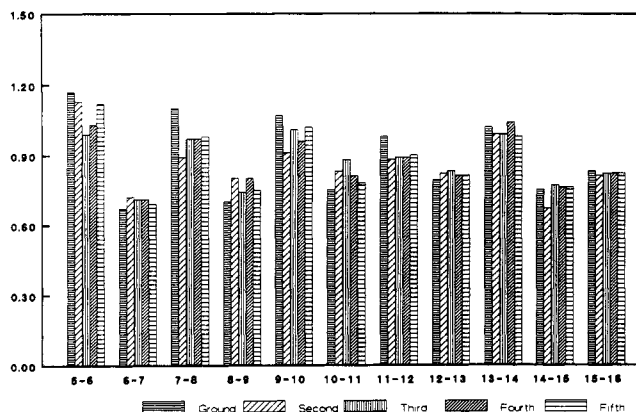


Figure 5. Overlap populations of the ground state and the excited state of PSBR between heavy atoms with the MRSD-CI(I) wave functions.

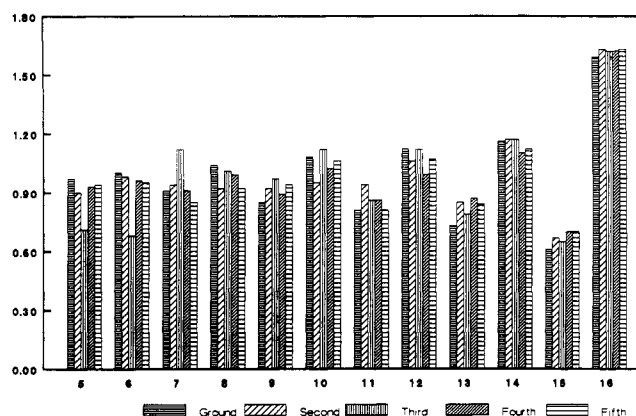


Figure 6. π -Electron distributions of the ground state and the excited states of PSBR with the MRSD-CI(I) wave functions. Locally defined π orbitals are chosen to be perpendicular to the plane determined by the carbon atom and the two neighboring carbon or nitrogen atoms and by the neighboring carbon and hydrogen atoms for C_5 and N_{16} .

Population analyses of the 1B_u state show small, but significant, charge transfer from the C_{11} to C_{13} portion to the C_8 to C_{10} portion of PSBR, confirming that this state is ionic. There is a large decrease of bond alternation in the region of C_7 to C_{12} , indicating some shifting of the double bonds of PSBR upon excitation.

For the third state, 2^1A_g , drastic charge transfer from the middle part of the molecule to the C_5 and C_6 region was observed. This large charge separation convinces us that this state is not the commonly thought covalent 1A_g state. In fact, it can be regarded as the result of the localized excitation on the $C_5=C_6$ double bond, which is twisted out of conjugation. Because of the charge building up on these two atoms, the bond order between them is greatly reduced. There is also some decrease of bond alternation in other parts of the molecule, but smaller in magnitude compared to 1B_u .

Compared to the ground state, the fourth state 3^1A_g has a similar charge distribution but a much smaller bond alternation from C_7 to C_{12} . These properties allow us to believe that this state is indeed the covalent 1A_g state. According to valence bond theory, there should be an overall reversal of bond alternation for this state. Because the twisting along the C_6-C_7 and $C_{12}-C_{13}$ bonds, decrease of the bond alternation concentrates in the C_7 to C_{12} region. The polarization of the fifth state, 4^1A_g , is also small. There is some decrease of the bond alternation in this state, but it is smaller than that in 3^1A_g . The nature of this state should also be diradical.

Population analysis in the π space was also performed with the p_π atomic orbitals, which are defined individually for each heavy atom so that they are perpendicular to the C-C-C plane, or the C-C-H, C-N-H planes for terminal atoms. As shown in Figure 6 and Figure 7, there is a stronger pattern of alternation in electron densities and overlap populations in the π space, indicating that most of the changes discussed in the previous paragraphs takes place in the π space. There are decreases of π bond alternations

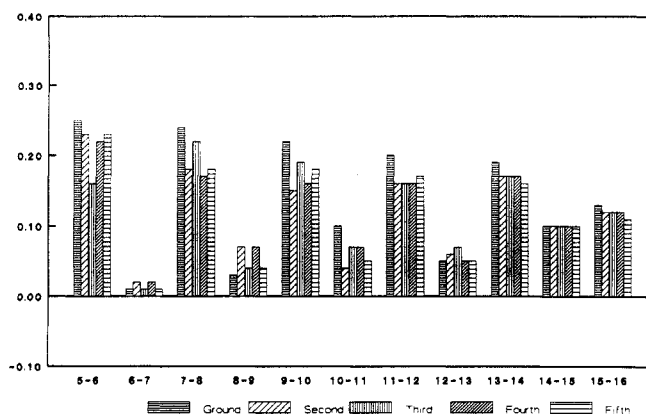


Figure 7. π -Overlap populations of the ground state and the excited states of PSBR with the MRSD-CI(1) wave functions. Locally defined π orbitals are chosen to be perpendicular to the plane determined by the carbon atom and the two neighboring carbon or nitrogen atoms and by the neighboring carbon and hydrogen atoms for C_5 and N_{16} .

TABLE V: Excited States of PSBR Calculated with π SDTQQS-CI/STO-3G^a

state	f	ΔE , eV	confign	coeff ^b
1		0.00 ^c	HF	0.8513
2	0.74	4.30	(π_6, π_{10}^*)	0.4216
			(π_6, π_{11}^*)	0.3805
3	0.23	5.58	$(\pi_6, \pi_7^*)^2$	0.2835
			(π_4, π_7^*)	0.2773
			(π_5, π_7^*)	0.2152
			$(\pi_6, \pi_7^*)(\pi_6, \pi_{10}^*)$	0.1858
			$(\pi_4, \pi_7^*)(\pi_6, \pi_9^*)$	0.1826
4	0.04	6.44	(π_3, π_7^*)	0.2391
			(π_5, π_{10}^*)	0.2246
			(π_6, π_8^*)	0.2204
			(π_5, π_{11}^*)	0.2028
			$(\pi_6, \pi_7^*)^2$	0.1906
			(π_6, π_7^*)	0.1700
5	0.15	6.74	$(\pi_6, \pi_7^*)^2$	0.3032
			(π_4, π_{10}^*)	0.2443
			(π_5, π_{10}^*)	0.2191
			(π_6, π_{11}^*)	0.2170
			(π_6, π_{10}^*)	0.2156
6	0.06	7.01	$(\pi_5, \pi_7^*)(\pi_6, \pi_8^*)$	0.3008
			$(\pi_5, \pi_7^*)(\pi_6, \pi_7^*)$	0.2431
			$(\pi_6, \pi_7^*)(\pi_6, \pi_8^*)$	0.2239
			$(\pi_5, \pi_7^*)(\pi_6, \pi_9^*)$	0.1815
			(π_4, π_7^*)	0.1782

^aSix-fold excitations are allowed in the π space, which consists of orbitals a_{29} , a_{38} , a_{40} , a_{41} , a_{42} , a_{43} , a_{44} , a_{45} , a_{46} , a_{47} , a_{48} , and a_{49} . See text for the definition of the π orbitals. The dimension of the CI matrix is 142878. ^bEnough configurations for each state are listed so that the square root of the sum of the square of the coefficients $(\sum c_i^2)^{1/2}$ is larger than 0.5. ^cGround-state CI energy: -473.17388 hartrees.

in the excited states, especially in 1B_u .

Discussion

Direct comparison of the excited states of PSBR and dodecahexaene was made by performing π CI calculations with the STO-3G basis set for both molecules. The same MMX geometry was taken for PSBR. The geometry of dodecahexaene was composed of the standard bond lengths and bond angles, namely, 1.46 Å for the C-C single bond, 1.35 Å for the C=C double bond, 1.08 Å for the C-H single bonds, and 120° for all bond angles. C_{2h} symmetry was imposed for the geometry and wave functions of dodecahexaene. A 6-fold-excitation CI, π SDTQQS-CI, for the 12 π electrons in the 12 π orbitals (with no more than 8 open shells) of PSBR and dodecahexaene was carried out. The 12 orbitals of PSBR with the most π character were selected from the population analysis of the ground RHFSCF orbitals with the locally determined p_π atomic orbitals. The six π MO's of PSBR are a_{29} , a_{38} , a_{40} , a_{41} , a_{42} , and a_{43} . The six π^* MO's are a_{44} , a_{45} , a_{46} , a_{47} , a_{48} , and a_{49} .

TABLE VI: Excitation Energies of Dodecahexaene Calculated with π SDTQQS-CI/STO-3G^a

state	ΔE , eV	confign	coeff ^b
ground	0.00 ^c	HF	0.8108
2^1A_g	4.86	$(\pi_6, \pi_7^*)^2$	0.4340
		$(\pi_5, \pi_7^*)(\pi_6, \pi_8^*)$	0.3037
1^1B_u	5.67	$(\pi_6, \pi_8^*)(\pi_6, \pi_7^*)$	0.3276
		$(\pi_6, \pi_7^*)(\pi_5, \pi_7^*)$	0.2941
		(π_4, π_7^*)	0.2793
3^1A_g	6.46	(π_3, π_7^*)	0.2791
		(π_6, π_{10}^*)	0.2570
		$(\pi_5, \pi_7^*)(\pi_6, \pi_8^*)$	0.2409
		(π_6, π_8^*)	0.1909
		$(\pi_4, \pi_7^*)(\pi_6, \pi_7^*)$	0.1748
4^1A_g	6.80	$(\pi_4, \pi_7^*)(\pi_6, \pi_7^*)$	0.2196
		$(\pi_5, \pi_7^*)(\pi_5, \pi_9^*)$	0.1964
		$(\pi_6, \pi_7^*)(\pi_6, \pi_9^*)$	0.1767
		$(\pi_5, \pi_9^*)(\pi_6, \pi_8^*)$	0.1765
		$(\pi_6, \pi_8^*)^2$	0.1752
		$(\pi_5, \pi_8^*)^2$	0.1730
		(π_4, π_8^*)	0.1556
		$(\pi_5, \pi_7^*)(\pi_6, \pi_8^*)$	0.1552
2^1B_u	7.10	(π_2, π_7^*)	0.2961
		(π_6, π_{11}^*)	0.2547
		$(\pi_6, \pi_7^*)(\pi_4, \pi_8^*)$	0.1668
		$(\pi_6, \pi_7^*)(\pi_6, \pi_{12}^*)$	0.1549
		$(\pi_5, \pi_7^*)(\pi_6, \pi_{11}^*)$	0.1501
		$(\pi_6, \pi_9^*)(\pi_6, \pi_8^*)$	0.1487
5^1A_g	7.47	$(\pi_5, \pi_7^*)(\pi_4, \pi_7^*)$	0.1406
		(π_1, π_7^*)	0.3533
		(π_6, π_{12}^*)	0.2824
		$(\pi_2, \pi_7^*)(\pi_6, \pi_7^*)$	0.1930
		$(\pi_3, \pi_7^*)(\pi_6, \pi_8^*)$	0.1833
3^1B_u	7.60	$(\pi_6, \pi_7^*)(\pi_3, \pi_7^*)$	0.2039
		$(\pi_6, \pi_7^*)(\pi_6, \pi_{10}^*)$	0.1951
		$(\pi_5, \pi_8^*)(\pi_6, \pi_8^*)$	0.1780
		$(\pi_5, \pi_7^*)(\pi_5, \pi_8^*)$	0.1657
		$(\pi_3, \pi_7^*)(\pi_6, \pi_9^*)$	0.1605
		(π_3, π_8^*)	0.1558
		$(\pi_6, \pi_8^*)(\pi_6, \pi_9^*)$	0.1528
		$(\pi_4, \pi_7^*)(\pi_5, \pi_9^*)$	0.1470
		(π_5, π_{10}^*)	0.1454

^aFor the 1A_g states, π SDTQQS-CI included 71766 spin-adapted configurations. For the 1B_u states, 85312 were included. ^bEnough configurations for each state are listed so that the square root of the sum of the square of the coefficients $(\sum c_i^2)^{1/2}$ is larger than 0.5. ^cGround-state energy: -457.04380 hartrees.

The first six states of PSBR were obtained variationally, and the relative energies and leading configurations are shown in Table V. The dominant configurations, as listed in Table V, of excited states 2, 4, and 5 are mostly one-electron excitations. Those of states 3 and 6 are mostly double excitations. States 3 and 6 may be regarded as covalent and states 2, 4, and 5 as ionic. Of course the ionic nature of a state cannot be fully determined by the analysis of electron excitations. By comparing Table II and Table V, one can relate state 2 to 1B_u , state 3 to $^3^1A_g$, and state 4 to 2^1A_g . A more flexible basis set and inclusion of σ excitations in CI stabilize the ionic states 1B_u and 2^1A_g states more (for about 0.7 eV and above) than the covalent state $^3^1A_g$ (for about 0.4 eV). The values of oscillator strengths calculated with STO-3G basis set are much smaller than those calculated with the SVP basis set.

Table VI lists the excited-state energies and dominant CI configurations for the first seven excited states of dodecahexaene. The first excited state is the covalent 1A_g state with a calculated excitation energy of 4.86 eV, which is in agreement with the published PPP results.³⁴ As expected, all the ionic states are poorly described and almost all dominant configurations for the excited states calculated involve two-electron excitations. In fact, the one-electron excited state 1B_u was not calculated to be among these first seven excited states. Furthermore, the oscillator strengths for the transitions from the ground state to the three

TABLE VII: Excitation Energies of Dodecahexaene Calculated with π Full-CI/STO-3G^a

state	<i>E</i>	confign	coeff ^b
ground	0.00 ^c	HF	0.8099
2 ¹ A _g	4.83	(π_6, π_7^*) ²	0.4322
		(π_5, π_7^*)(π_6, π_8^*)	0.3027
1 ¹ B _u	5.66	(π_6, π_8^*)(π_6, π_7^*)	0.3266
		(π_6, π_7^*)(π_5, π_7^*)	0.2930
		(π_4, π_7^*)(π_5, π_7^*)	0.2785
3 ¹ A _g	6.43	(π_3, π_7^*)	0.2778
		(π_6, π_{10}^*)	0.2561
		(π_5, π_7^*)(π_6, π_8^*)	0.2401
		(π_6, π_8^*) ²	0.1902
		(π_6, π_7^*) ²	0.1741
4 ¹ A _g	6.77	(π_4, π_7^*)(π_6, π_7^*)	0.2186
		(π_5, π_7^*)(π_5, π_9^*)	0.1953
		(π_6, π_7^*)(π_6, π_9^*)	0.1758
		(π_6, π_8^*)(π_5, π_9^*)	0.1753
		(π_6, π_8^*) ²	0.1743
		(π_5, π_8^*) ²	0.1717
		(π_4, π_8^*)(π_6, π_8^*)	0.1553
		(π_5, π_7^*)(π_6, π_8^*)	0.1546
2 ¹ B _u	7.08	(π_2, π_7^*)	0.2950
		(π_6, π_{11}^*)	0.2536
		(π_6, π_7^*)(π_4, π_8^*)	0.1663
		(π_6, π_7^*)(π_6, π_{12}^*)	0.1547
		(π_5, π_7^*)(π_6, π_9^*)	0.1498
		(π_6, π_9^*)(π_6, π_8^*)	0.1481
		(π_5, π_7^*)(π_4, π_7^*)	0.1401
5 ¹ A _g	7.43	(π_1, π_7^*)	0.3501
		(π_6, π_{12}^*)	0.2816
		(π_3, π_7^*)(π_6, π_8^*)	0.1867
		(π_6, π_7^*)(π_2, π_7^*)	0.1802
3 ¹ B _u	7.58	(π_6, π_7^*)(π_3, π_7^*)	0.2028
		(π_6, π_7^*)(π_6, π_{10}^*)	0.1939
		(π_5, π_8^*)(π_6, π_8^*)	0.1779
		(π_5, π_7^*)(π_5, π_8^*)	0.1651
		(π_3, π_7^*)(π_6, π_9^*)	0.1599
		(π_3, π_8^*)	0.1554
		(π_6, π_9^*)(π_6, π_8^*)	0.1527
		(π_5, π_9^*)(π_4, π_7^*)	0.1466
		(π_5, π_{10}^*)	0.1454

^a For the ¹A_g states, π full-CI included 110 804 spin-adapted configurations. For the ¹B_u states, 110 032 were included. ^b Enough configurations for each state are listed so that the square root of the sum of the square of the coefficients ($\sum c_i^2$)^{1/2} is larger than 0.5. ^c Ground-state energy: -457.044 20 hartrees.

¹B_u states that did fall into the first seven excited states are close to zero. Full CI in the π space with limitations to eight open shells was also carried out for dodecahexaene. As shown in Table VII, the excitation energies and wave functions are almost identical with those calculated by π SDTQQS-CI, confirming that the limitation of describing the excited states is indeed from the lack of flexibility of the minimal basis set, not from the truncation of CI.

Despite the severe defect of the minimal basis set in describing highly polar excited states, comparisons between dodecahexaene and PSBR based on these results are informative. It can be seen that, because PSBR is charged, its spectrum is very different from that of dodecahexaene. There is little correlation between the excited states of these molecules. The only resemblance in the wave functions may be found between the 2¹A_g state of dodecahexaene and state 3 of PSBR, with the latter being 0.9 eV lower in energy. This large difference in spectra implies that the excited-state properties of polyenes cannot be directly extended to PSBR.

Population analyses of PSBR with the π SDTQQS-CI/STO-3G wave functions for the excited states show different degrees of decrease in bond alternation (Figure 8 and Figure 9). The total overlap population also decreases from the ground state to the higher excited states. All carbon atoms of dodecahexaene have almost unity in the π population of all states calculated. There is also a decrease in overlap populations from the ground state to the excited states of dodecahexaene (Figure 10).

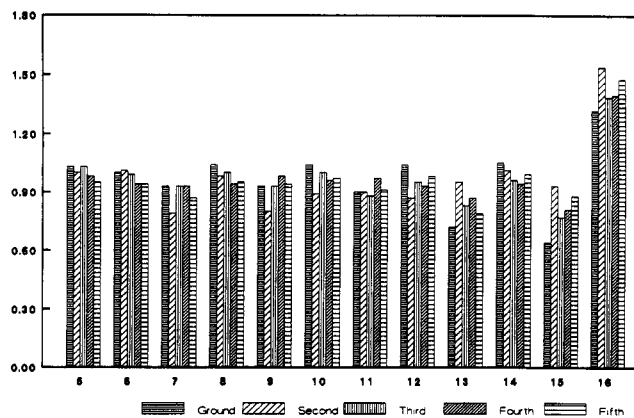


Figure 8. π -Electron distributions of the ground state and the excited states of PSBR with the π SDTQQS-CI/STO-3G wave functions. Locally defined π orbitals are chosen to be perpendicular to the plane determined by the carbon atom and the two neighboring carbon or nitrogen atoms and by the neighboring carbon and hydrogen atoms for C₅ and N₁₆.

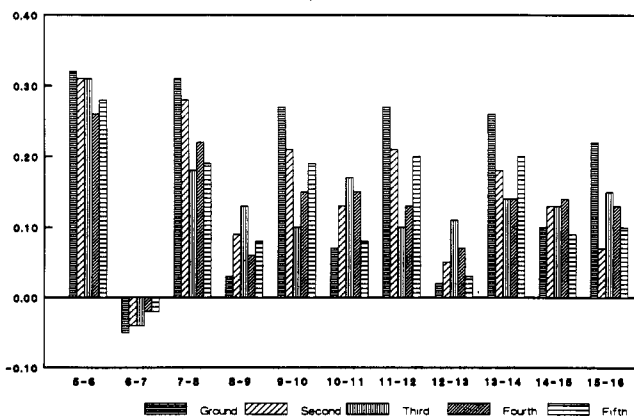


Figure 9. π -Overlap populations of the ground state and the excited states of PSBR with the π SDTQQS-CI/STO-3G wave functions. Locally defined π orbitals are chosen to be perpendicular to the plane determined by the carbon atom and the two neighboring carbon or nitrogen atoms and by the neighboring carbon and hydrogen atoms for C₅ and N₁₆.

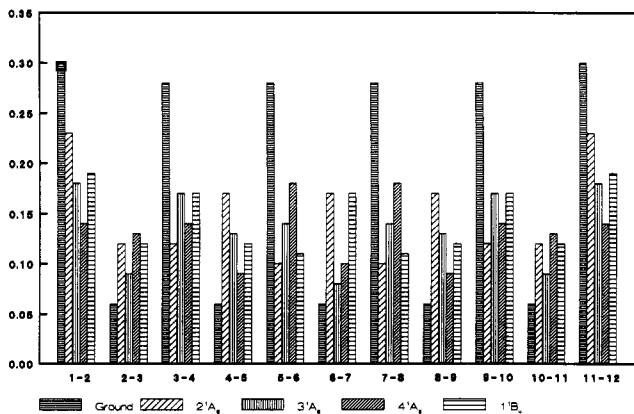


Figure 10. π -Overlap populations of the ground state and the excited states of dodecahexaene with the π SDTQQS-CI/STO-3G wave functions.

From the charge distribution of the ground state of PSBR with both MRSD-CI(I)/SVP and SDTQQS-CI/STO-3G wave functions, we predict that the position of the primary counterion should be next to the NH₂⁺ and the adjacent CH groups. The existence of secondary counterions near C₁₁ and C₁₃ is also likely. It should be noted that, upon excitation to the ¹B_u state, the charge densities of PSBR are greatly reduced on C₁₁ and C₁₃ but essentially unchanged on C₁₅ and N₁₆, implying that the largest geometry distortion in the C₁₁ to C₁₃ region is favored.

For years semiempirical methods have been largely exploited in reproducing the experimental values of excitation energies of PSBR. INDO-CISD⁴ and PPP-CISD^{6,35-37} calculated the excitation energy between 2.2 and 2.5 eV for the 1B_u state and between 3.2 eV and 3.5 eV for the 1A_g state. These results agree well with the maximum absorption of PSBR (2.58 eV) and the two-photon-absorption peak of the 1A_g state (2.83 eV)^{14,38} in solution.

The difficulty of treating PSBR with ab initio method is apparent. It is mostly because of the large correlation energy of the molecule relative to its excitation energies. The correlation energy available from the MRSD-CI(I) is 18 eV for the ground state, whereas the excitation energy for the 1B_u is only 3.8 eV. The size of the molecule forced us to truncate a large portion of the CI matrix out of the variational calculations. Extrapolation often brings large uncertainties in the correlation energies of the individual states when the correlation energy truncated is as high as 50%. Meanwhile, to describe the excited states properly, diffuse functions are necessary,³⁹ especially when the excited state is highly polar.

Nevertheless, our ab initio results agree that the 1B_u state is the lowest excited state. The excitation energy of 2.7 eV calculated is in agreement with the experimental results. Besides the obvious limitation in basis set and configuration interaction, there are two other factors that may contribute to the final determination of the excitation energy of the 1B_u state. One is the neglect of the saturated ionone ring and the methyl groups of PSBR. Inclusion of these groups often lowers the excitation energy. The other factor is the neglecting of the counterions in solution, which can increase the excitation energy, as demonstrated by some theoretical and experimental studies.^{6,7,16,40} From the wave function of the 1B_u state, one can see that there is a large mixing of higher excitations into 1B_u . This mixing has been assumed to be important in pushing down the excited-state potential energy surface upon the cis-trans geometric isomerization of PSBR^{15,16}.

In PSBR all states are mixed because of the lack of symmetry. Population analysis shows that the second excited state is highly

localized. On the basis of the fact that the dominant configuration of this state is $(-2,+1)$ and that of the $(-2,+1)$ configuration of the polyenes is totally symmetric, it seems that this state is 1A_g -like. This state, however, does not correspond to the covalent 1A_g state of polyenes, which have the two-electron-excitation configuration, $(-1,+1)^2$, as the dominant configuration.

The results of MRSD-CI(I) and MRSD-CI(II) show some contribution of the double-excitation configuration $(-1,+1)^2$ to the wave functions of the third excited state, indicating that this state is 1A_g -like. The other leading configurations, none of them being dominant, are single-electron excitations. The multiconfigurational nature of this state suggests that the third excited state is the covalent 1A_g -like state, a conclusion supported by the small oscillator strength calculated for this state (0.13) and its decreased bond alternation. The fourth excited state is also multiconfigurational and has a wave function similar to that of the third.

Conclusions

Ground-state population analysis shows that the positive charge of the isolated PSBR cation is largely localized on N₁₆, C₁₅, C₁₃, and C₁₁, which indicates that counterions in the vicinity of these atoms could be a factor in regulating the absorption maximum of rhodopsin. The bonding characters of the excited states of PSBR are mixed. Only a vague line can be drawn between 1A_g -like and 1B_u -like states and between the ionic and the covalent states. The first excited state of PSBR is 1B_u -like and is more polarized than the ground state. Although the second excited state was found to be 1A_g -like, it is ionic and highly localized. It is the third excited state in these calculations that corresponds to the commonly referred covalent 1A_g state. The transition from the ground state to the 1B_u -like state is calculated to be strongly allowed, whereas the oscillator strengths for the other excited states are small.

Our best estimate of the excitation energy for the 1B_u state of PSBR with the absence of substituents and counterions is 2.7 ± 0.5 eV. Although this state is mostly a single excitation, it mixes with some higher excitation character, which could be important in understanding the fast geometric isomerization of PSBR upon light absorption. Comparison between PSBR and dodecahexaene with the results of the SDTQQS-CI/STO-3G calculations indicates little resemblance of the excited-state wave functions and energies, implying that the excited-state properties of polyenes cannot be directly extended to PSBR.

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