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Photoisomerization of *p*-(Dimethylamino)-*β*-chlorostyrene: A Low Temperature Matrix Isolation FTIR Study

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The low-temperature matrix isolation technique in combination with FTIR spectroscopy, has been used to study the trans−cis photoisomerization of *p*-(dimethylamino)-*β*-chlorostyrene (DMACS). The highly dominant form of the compound immediately after deposition in argon matrix has been identified, by comparison of its experimental infrared spectrum with that calculated at the DFT(B3LYP)/6-31G** level, as the trans isomer. Upon UV irradiation of the matrix, a photoreaction was observed resulting in the appearance of a new IR spectrum corresponding to the photoproduct. By comparison with the theoretically predicted spectra, the photoproduct was identified as the cis form of DMACS. Cross-sections of the potential energy surfaces (PES) along the $C_1-C_{10}{=}C_{11}-Cl$ torsional coordinate in the ground (S_0) as well as in the lowest excited singlet (S_1) states were generated using the semiempirical (AM1) method. Although the relative energies of the two isomers are quite close (4.6 kJ mol^{-1}, MP2/6-31G** calculation) in the ground state, the PES reflects that attainment of the equilibrium in the distribution of the two isomers is restricted because of a large activation barrier. The simulated PES, however, corroborates a trans → cis photoisomerization process involving the participation of the S_1 state.

Introduction

Photoisomerization involving rotation of groups (or atoms) around a double bond in olefinic compounds belongs to the most important group of processes in photochemistry. The trans−cis photoisomerization of styrene/derivatives, in particular, have long been the subject of immense research because of the mechanistic aspect as well as the potential of these molecules as charge carriers.[1−8] The important role of the isomerization process of styrene/s in nonradiative deactivation is manifested by the fact that the lifetime of the electronically excited styrene depends on the excitation energy. The lifetime of the excited state gradually decreases with increasing excitation energy. This effect is attributed to photoisomerization around the ethylenic double bond leading to an additional channel of excitation energy dissipation.[9−11] The decay behavior of the excited state in styrene can be modulated by a suitable choice of the substituent groups.[8]

In principle, depending on the specificity of a molecular system, the following two situations may arise for the photoisomerizable systems. In the ground state, two isomers (trans and cis) may remain in equilibrium, provided they do not differ very much in energies (thermodynamic criterion), and the activation energy for the interconversion process is attainable (kinetic criterion) at ambient temperature. In such a case, UV irradiation leads to a shift in the equilibrium in favor of a particular form through photoisomerization till the irradiation source is in operation. In the absence of irradiation, the system reverts back to the original ground state distribution. On the other hand, when there is a sufficiently high activation barrier for the interconversion process in the ground state, unattainable under the experimental conditions, the composition of the sample is dictated by the way of its preparation. Photoisomerization, in this case, leads to an interconversion through the excited singlet state (S_1) because of the reduced activation energy in this electronic state. Depending on the relative position of the potential energy surface (PES) of the S_1 state and the ground state (S_0) in the conical intersection (CIX) zone, this phototransformation may be unidirectional or bidirectional, depending on the excitation wavelength.[12]

Matrix isolation combined with FTIR spectroscopy is an established technique, which provides structural information about molecular systems.[13,14] A comparison of the experimental infrared spectrum with its theoretically simulated counterpart allows a reliable identification of the species present in the matrix. Recently, syn−anti photoisomerization reactions of N^4-hydroxycytosines and benzaldoxime, a process quite similar to that studied in the present work, have been observed in the matrix isolated systems.[12,15] Prompted by these works, we investigated the photoisomerization reaction of a new molecular system, *p*-(dimethylamino)-*β*-chlorostyrene, isolated in a low-temperature Ar matrix. The infrared spectra of the substrate and the product of the photoreaction have been identified by comparison with the spectra theoretically calculated for the trans and cis isomers, using the density functional theory (DFT) approach. A semiempirical simulation of the PES in the S_0 and S_1 states supports the photoreaction through the involvement of the S_1 state.

Experimental Section

p-(Dimethylamino)-*β*-chlorostyrene (DMACS) was synthesized from *p*-dimethylaminobenzaldehyde (DMABA) following

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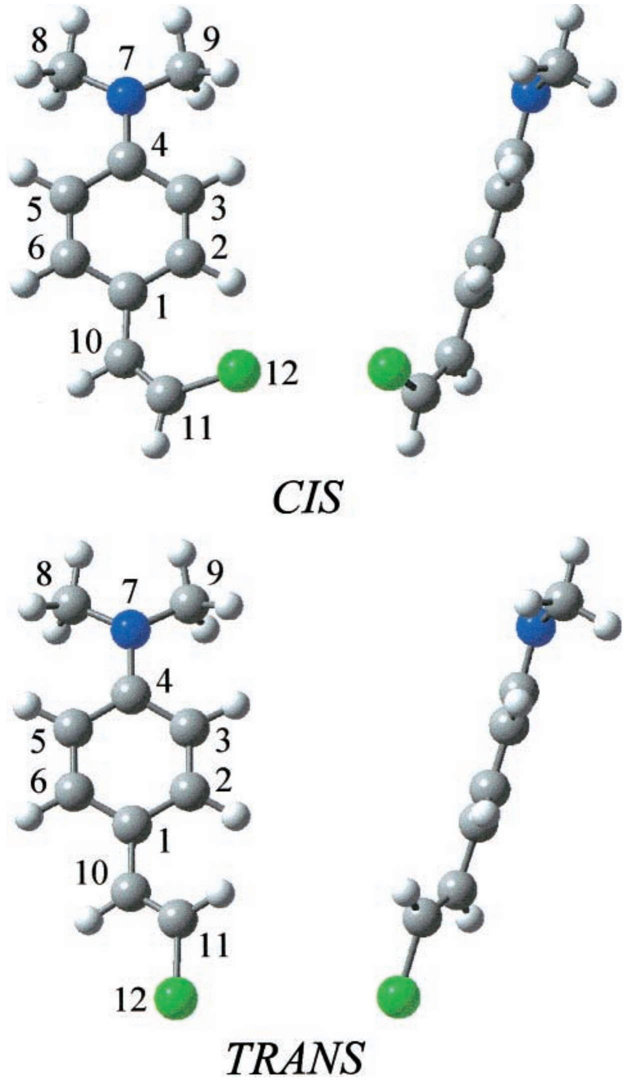

Figure 1. MP2/6-31G** optimized structures of the trans and cis isomers of DMACS. The double bond exists between two carbon atoms numbered as 10 and 11. The nitrogen atom is numbered with 7 (blue), and chlorine atom is numbered with 12 (green).

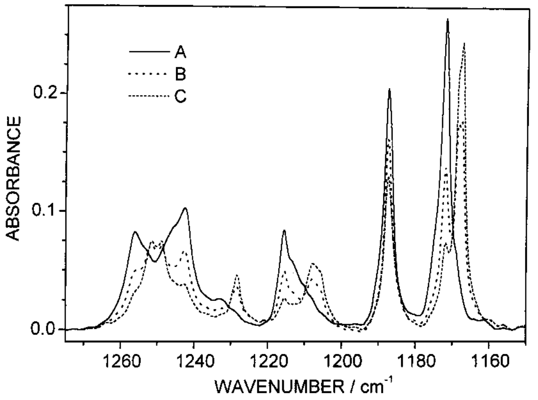

Figure 2. A portion of the IR spectrum of DMACS isolated in the Ar matrix at 9 K. A, after deposition of the matrix; B, after 30 min of irradiation; C, after 2 h of irradiation.

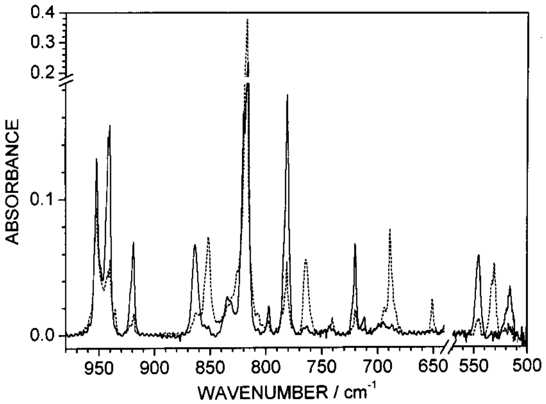

Figure 3. A portion of the IR spectrum of DMACS isolated in the Ar matrix at 9 K. Solid line, after deposition of the matrix; dotted line, after 2 h of irradiation.

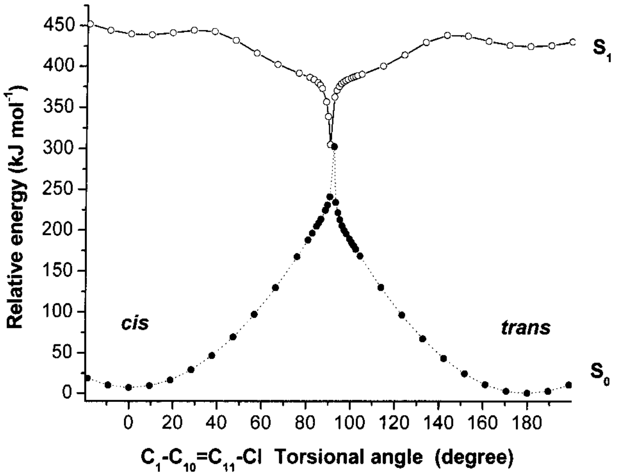

Figure 4. Potential energy of DMACS in the S_0 and S_1 states as a function of $C_1{-}C_{10}{=}C_{11}{-}Cl$ torsional angle. For notations of the atoms, see Figure 1.

the procedure described by Akiyama et al.[16,17] The compound was purified by recrystallization from a 1:1 mixture of *n*-hexane and diethyl ether, and the purity of the compound was checked by thin-layer chromatography (TLC).

Low-temperature matrixes were prepared by heating a sample of DMACS to about 310 K in a tiny oven placed in the vacuum chamber of the cryostat. The vapor of the compound was deposited, together with a large excess of the matrix gas (Ar), onto a CsI window, mounted on the cold tip (down to 9 K) of the APD Cryogenics DE−202A closed-cycle helium refrigerator. Argon (99.9999% purity) was supplied by Air Liquide. Infrared spectra were recorded, with a resolution of 0.5 cm^{-1}, on a Mattson Infinity 60AR FTIR spectrometer, equipped with SiC globar source, KBr beam-splitter and DTGS mid-IR detector. The matrixes were irradiated, through the outer KBr window of the cryostat, with an unfiltered 150 W xenon lamp (Osram XBO 150 W/CR OFR). No annealing of the matrixes occurred during the irradiation, indicating that there was no significant increase in temperature of the matrix samples.

Computational Section

Geometries of the trans and cis isomers of DMACS were optimized at MP2/6-31G** and DFT(B3LYP)/6-31G** levels of theory using the Gaussian 98 software.[18] The structures optimized at MP2 level are presented in Figure 1. At the DFT optimized geometries, harmonic frequencies (considering ^{35}Cl only) and IR intensities were calculated for both the trans and cis isomers of the compound. To correct for the anharmonicity and the neglected part of the electron correlation effect, the calculated frequencies were scaled by a single factor of 0.97.

To simulate the PES for the isomerization process in S_0 and S_1 states, the semiempirical (AM1) method has been adopted. HyperChem 6.01 software was used for the purpose. Photoi-

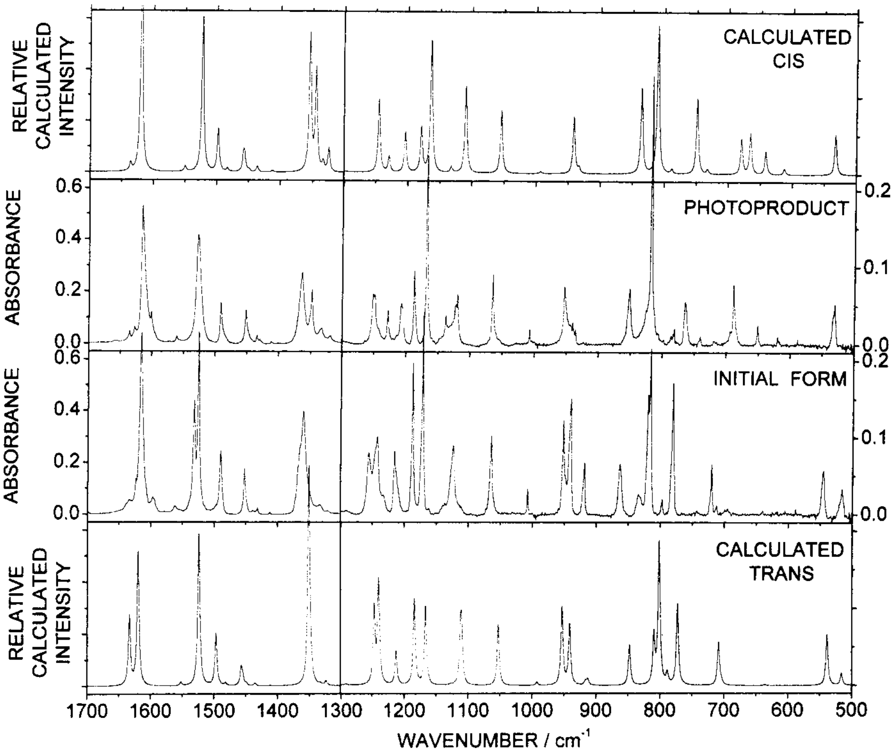

Figure 5. Comparison of the experimental IR spectra of the substrate and the photoproduct with the calculated spectra (at the DFT(B3LYP)/6-31G** level) for the trans and cis isomers of DMACS. Note the change of the ordinate scale at 1300 cm^{-1}. The calculated frequencies are scaled with a uniform scale factor 0.97.

somerization through T_1 has not been considered, because intersystem crossing is expected to be inefficient. The C_1—C_{10}=C_{11}—Cl torsional angle (see Figure 1) has been chosen as the reaction coordinate. For the generation of the cross-sections of the PES for the isomerization process, we have optimized the molecular geometry with various preset values of the reaction coordinate. AM1-SCI was then applied to obtain the energies of the species on the trajectory of the reaction in the two electronic states. The method also gives the calculated oscillator strengths for the $S_0 \rightarrow S_1$ absorption for the trans and the cis isomers of DMACS. All of the configurations (ca. ∼120) within an energy window of 13.5 eV from the ground state (for single electronic transitions only) have been taken into account.

Results and Discussion

Two fragments of the IR spectrum of DMACS isolated in low-temperature Ar matrix are presented in Figures 2 and 3. Upon UV irradiation, the intensities of the bands in the initial spectrum decreased considerably with a concomitant appearance of a new spectrum corresponding to a photoproduct.

Because of the structural similarity between the trans and the cis isomers of the molecular system (apart from the ethylenic fragment), some of the bands in the spectrum of the photoproduct coincide with the corresponding bands in the spectrum of the initial form (e.g., bands at 1187.7 and 952.0 cm^{-1}, see Figures 2 and 3). On the other hand, some bands in the spectra of the substrate and the photoproduct are clearly distinct in frequencies (e.g., 918.9, 720.3, 545.6, and 516.3 cm^{-1} for the initial form and 764.5, 689.1, 651.2, and 531.2 cm^{-1} for the photoproduct, see Figure 3). This allows clear observation of the progress of the photoreaction. However, in the majority of the cases, the bands of the photoproduct overlap partially with the bands of the initial form. Following irradiation of DMACS in the matrix, many isosbestic points were observed throughout the IR spectra after different times of irradiation (Figure 2). Existence of the isosbestic points (several of them can be seen in Figure 2) confirms a one to one conversion from the substrate to the product and rules out any photodegradation of the compound during the reaction.

Theoretical calculations of the relative ground-state energies of the trans and cis isomers of DMACS (carried out at the MP2/6-31G** level) predict the trans form being more stable by only 4.6 kJ mol^{-1}. However, the population ratio of trans and cis forms of the compound in the ground state is not necessarily governed by this energy difference. The very high activation barrier for rotation around the ethylenic double bond can preclude population of the two forms which would be given by the Boltzmann distribution. For the present molecular system, AM1 calculation predicts the barrier as high as 250 kJ mol^{-1} (vide supra) which would rule out any thermal interconversion at moderate temperature. In the present experiment, a temperature of 310 K was used to evaporate DMACS during the matrix deposition (refer to the Experimental Section). This temperature is far too low to promote crossing of such a high barrier. Activation barriers similar to that calculated in the present work are typical for styrene and its derivatives.[10] The relative abundance of the trans and cis isomers in the sample is, thus, dependent on the way the compound was synthesized and purified. We have used two different samples of DMACS, one being the direct product of the synthesis and the other one recrystallized as described in the Experimental Section. The same IR bands were observed in the spectra collected after deposition of either of the samples into the argon matrix. However, in the two experiments, the IR intensities of a set of weaker bands were different, with respect to the strong bands in the spectrum of the dominating form. This behavior allowed differentiation between the spectra of the dominating isomer and the minor form. The spectra growing upon UV irradiation correspond exactly to the spectra of the minor form of the compound observed just after deposition. All the stronger bands in the spectrum of the photoproduct have their counterparts appearing as low (or very low) intensity bands already existing in the spectra recorded before irradiation. On the basis of the comparison with the theoretically predicted spectra (to be discussed in a forthcoming section), the form dominating in the sample before irradiation has been identified as the trans isomer, whereas the product of the photoreaction as the cis isomer.

The photoreaction observed for the matrix-isolated DMACS progressed continuously during the irradiation process. After prolonged (2 h) irradiation of the sample, the reaction led to nearly total consumption of the initial trans isomer. This suggests that the photostationary state under the experimental conditions is shifted very much in favor of the photoproduct (cis isomer). Although Stepanenko et al. observed the photostationary state for benzaldoxime, pyridine-4-aldoxime,[12] and *N*^{4}-hydroxycytosine[15] leading to mixture of syn and anti isomers, this is not a rule for all molecular systems. Photochemical equilibrium is possible if the PES along the coordinate of the torsional angle responsible for the photoisomerization are, in a good approximation, symmetric in both the ground (S_0) and the excited (S_1) states.[19] In such a situation, after excitation to the S_1 state, the system may relax with nearly equal probability to either of the isomers.[15] However, if the PES are distorted from the symmetrical shape, then the direction of the reaction and the ratio of the two isomers in the photoproduct will change remarkably. A difference between the absorption coefficients of the two species at the wavelength of the exciting radiation must be taken into account as well. For the DMACS system, the AM1-SCI predicted oscillator strengths for the $S_0 \rightarrow S_1$ transition are not much different for the trans and cis isomers (being 0.40 and 0.30, respectively). Hence, the asymmetry of the PES must play an important role in controlling the final composition of the sample after prolonged irradiation.

The simulated PES for the trans − cis photoisomerization reaction in the ground and the first excited singlet (S_1) states are shown in Figure 4. As mentioned above, the trans isomer is slightly more stable than the cis isomer. The ground-state PES shows a large activation barrier (ca. ~250 kJ mol^{-1}) ruling out the possibility of the isomerization process in the ground state. As is evident from the figure, the barrier for interconversion of the isomers is reduced drastically in the excited state.

In the S_1 state, the barriers between the local minima corresponding to the trans and cis isomers and the global minimum are only 13.4 and 5.7 kJ mol^{-1}, respectively. This small amount of excess energy is achievable under the conditions of the present experiment. The simulated PES produces a conical intersection (CIX) suggesting a route for the nonradiative deactivation of the excited species through the isomerization process. Existence of a CIX is quite common for such isomerization reactions.[20−22] A careful observation of the PES near the CIX reveals that the PES in the S_0 and S_1 states are not perfectly symmetric in this zone. The minimum on the S_1 surface is slightly shifted (with respect to the maximum on the S_0 surface) toward the cis isomer. This asymmetry at the crossover point predicts the direction of the photoisomerization as trans → cis. It also suggests that a total conversion of the trans isomer into the cis form, rather than a photostationary point, should be the final stage of the photoreaction. Both of these predictions are consistent with the experimental observations.

The experimental IR spectra of the substrate and the photoproduct were separated by electronic subtraction. In particular, to obtain the spectrum of the photoproduct, the initial spectrum was multiplied by such a factor that the remainder of the bands of the initial (trans) form vanish after subtraction from the spectrum collected after UV irradiation. The best result was obtained using a factor equal to 0.18, indicating that more than 80% of the initial form was converted into the photoproduct after 2 h of irradiation. The experimental spectra of the two substances (reactant and photoproduct) are compared with the spectra of the trans and cis isomers of DMACS calculated at the DFT(B3LYP)/6-31G** level (Figure 5).

Although because of structural similarity (apart from the ethylenic fragment) of these forms their IR spectra do not differ much, there are several features distinguishing them clearly. The calculated spectra for both trans and cis forms of DMACS are given in Tables S1−S3 (Supporting Information), where full theoretical band assignments based on the potential energy distribution (PED) obtained from the normal coordinate analysis are presented.

In the lowest frequency region, two bands (at 538.8 and 516.3 cm^{-1}; DFT; scaled frequencies) are predicted for the trans isomer, whereas only one band (at 532.9 cm^{-1}) was expected for the cis form. A nice correspondence was found between this prediction and the bands present in the respective range of the experimental spectra. Two bands (at 545.6 and 516.3 cm^{-1}) were observed for the initially abundant form and only one (at 531.2 cm^{-1}) for the photoproduct. In a densely spaced IR spectrum like that of DMACS, a region free of any intense bands can be even more characteristic than the presence of a band at a certain frequency. No IR bands of significant intensity were predicted for the trans isomer of the compound in the range 700−560 cm^{-1}. The corresponding region free of any intense band has been observed in the experimental spectrum recorded before irradiation of the matrix (see Figure 5). On the contrary, in the experimental spectrum of the photoproduct, several bands appear in this frequency range. At slightly higher frequencies, two bands are observed at 720.3 and 781.3 cm^{-1} in the spectrum recorded before irradiation. This pair corresponds well to the bands predicted for the trans isomer at frequencies 708.4 and 772.6 cm^{-1}, respectively. Between these frequencies no bands are either predicted (for the trans isomer) or observed in the initial spectrum. However, two bands appear at 764.5 and 740.8 cm^{-1} in the experimental spectrum of the photoproduct in accordance with the spectrum predicted for the cis isomer (calculated frequencies, 748.8 and 732.7 cm^{-1}; see Figure 5). Also in the higher frequency range, the predicted spectrum of the trans form fits much better the experimental spectrum of the initial form than the spectrum of the photoproduct. The two bands, predicted for the trans isomer, at 1633.0 and 1619.4 cm^{-1} seem to overlap in the experimental spectrum leading to one band at 1616 cm^{-1}. Similarly, as for the trans isomer, agreement has been found between the higher frequency regions of the predicted spectrum of the cis isomer and the experimental spectrum of the species appearing upon UV irradiation.

All of the above reasons give strong support to the validity of the assignment of the trans and cis forms of DMACS respectively to the initially abundant form of the compound and to the form produced photochemically.

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Supporting Information Available: Tables S1, S2, and S3 (supplementary material) provide full assignment of the calculated IR spectra of the cis and the trans forms of the compound DMACS. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Waldeck, D. H. *Chem. Rev*. **1991**, *91*, 415.

(2) Arai, T.; Tokumaru, K. *Chem. Rev*. **1993**, *93*, 23.

(3) Gruen, H.; Görner, H. *Z. Naturforsch*. **1983**, *38a*, 928; *J. Phys. Chem*. **1989**, *93*, 7144.

(4) Görner, H.; Kuhn, H. J. *Adv. Photochem*. **1995**, *19*, 1.

(5) Maeda, Y.; Okada, T.; Mataga, N. *J. Phys. Chem*. **1984**, *88*, 2714.

(6) Letard, J. F.; Lapouyade, R.; Rettig, W. *J. Am. Chem. Soc*. **1993**, *115*, 2441.

(7) Il'ichev, Y. V.; Kühnle, W.; Zachariasse, K. A. *Chem. Phys*. **1996**, *211*, 441.

(8) Raj Gopal, V.; Jayatirtha Rao, V.; Saroja, G.; Samanta, A. *Chem. Phys. Lett*. **1997**, *270*, 593.

(9) Hui, M. H.; Rice, S. A. *J. Chem. Phys*. **1974**, *61*, 833.

(10) Syage, J. A.; Lambert, W. R.; Felker, P. M.; Zewail, A. H.; Hochstrasser, R. M. *Chem. Phys. Lett*. **1982**, *88*, 266.

(11) Syage, J. A.; Al Adel, F.; Zewail, A. H. *Chem. Phys. Lett*. **1983**, *103*, 15.

(12) Stepanenko, T.; Lapinski, L.; Nowak, M. J.; Adamowicz, L. *Vibr. Spectrosc*. **2001**, *26*, 65.

(13) Almond, M. J.; Downs, A. J. *Adv. Spectrosc.* **1989**, *17*, 1.

(14) Dunkin, I. R. *Matrix-Isolation Techniques: A Practical Approach*; Oxford University Press: Oxford, U.K., 1998.

(15) Stepanenko, T.; Lapinski, L.; Sobolewski, A.; Nowak, M. J.; Kierdaszuk, B. *J. Phys. Chem. A*. **2000**, *104*, 9459.

(16) Akiyama, S.; Nakatsuji, S.; Yoshida, K.; Nakashima, K.; Hagiwara, T.; Tsuruta, H.; Yoshida, T. *Bull. Chem. Soc. Jpn*. **1983**, *56*, 361.

(17) Chattopadhyay, N.; Serpa, C.; Pereira, M. M.; de Melo, J. S.; Arnaut, L. G.; Formosinho, S. J. *J. Phys. Chem. A* **2001**, *105*, 10025.

(18) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Baboul, A. G.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Andres, J. L.; Gonzalez, C.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98*, revision A.9; Gaussian, Inc.: Pittsburgh, PA, 1998.

(19) Klessinger, M.; Michl, J. *Excited States and Photochemistry of Organic Molecules*; VCH: New York, 1995.

(20) Amatatsu, Y. *Chem. Phys. Lett*. **2001**, *344*, 200; **1999**, *314*, 364.

(21) Bearpark, M. J.; Bernardi, F.; Clifford, S.; Olivucci, M.; Robb, M. A.; Vreven, T. *J. Phys. Chem. A* **1997**, *101*, 3841.

(22) Molina, V.; Merchán, M.; Roos, B. O.; Malmqvist, P.-Å. *Phys. Chem. Chem. Phys*. **2000**, *2*, 2211.