ELSEVIER

Journal of Photochemistry and Photobiology A: Chemistry 105 (1997) 325–328

Journal of
PHOTOCHEMISTRY
AND
PHOTOBIOLOGY
A:CHEMISTRY

Mechanism of photoinduced intramolecular charge transfer in aminobenzethynes: an ab initio study

Andrzej L. Sobolewski [a,*], Wolfgang Domcke [b]

[a] *Institute of Physics, Polish Academy of Sciences, 02 668 Warsaw, Poland*
[b] *Institute of Theoretical Chemistry, Heinrich-Heine-University, D-40225 Düsseldorf, Germany*

Received 20 August 1996; revised 28 October 1996; accepted 11 December 1996

Abstract

Ab initio electronic structure calculations were performed to characterize the charge transfer (CT) process in benzethyne (BE), 4-aminobenzethyne (ABE) and 4-dimethylamino-benzethyne (DMABE). The Hartree–Fock (HF), configuration interaction scheme (CIS), complete active space self-consistent field (CASSCF) and CASPT2 (multiconfigurational second-order perturbation theory taking CASSCF function as a reference) methods were employed. Geometry optimization of the CT state at the CIS level predicts a planar configuration with a trans bent ethyne group to be the lowest excited singlet state in all systems. The significant stabilization of the CT state in the BE series can be understood as arising from the rehybridization of the carbon atoms of the ethyne group on transfer of an electron. The calculation of the relative energy of the locally excited state and the relaxed CT state using the CASPT2 method reveals that the intramolecular CT process is exothermic in ABEs under isolated molecule conditions, in contrast with the much studied aminobenzonitriles, where interaction with a polar solvent is required for sufficient stabilization of the CT state. Therefore BE and its amino derivatives potentially offer unique opportunities for the investigation of photoinduced intramolecular CT in isolated molecules. © 1997 Elsevier Science S.A.

Keywords: Ab initio study; Aminobenzethynes; Photoinduced intramolecular charge transfer

1. Introduction

Photoinduced intramolecular charge transfer (CT) is one of the most fundamental and widely occurring processes in liquid phase photochemistry. A characteristic signature of the CT process is the observation of dual fluorescence [1]. According to the well-known twisted intramolecular charge transfer (TICT) model of Grabowski and coworkers [2,3], the CT is promoted by an out-of-plane twisting of the donor and acceptor moieties. The investigation of numerous so-called TICT molecules has shown that the photoinduced CT process depends very sensitively on the polarity of the solvent [4].

Despite many investigations, the mechanism of the CT process responsible for dual fluorescence in solution is still not well understood (e.g. see Ref. [5]). The complexity of the problem arises from the fact that an extensive intramolecular geometric rearrangement, a pronounced change in the electronic structure and the dielectric response and thermal fluctuations of the solvent are involved.

It is therefore attractive to investigate the intramolecular CT process in isolated molecules as this will eliminate the complications arising from solvation dynamics. In this work, we present results of ab initio electronic structure calculations on benzethyne (phenylacetylene) and its amino and dimethylamino derivatives. Our results suggest that these molecules should be promising candidates for the spectroscopic investigation of photoinduced CT in isolated molecules.

2. Results and discussion

In this study, we consider three molecular systems: benzethyne (BE) and its 4-amino (ABE) and 4-dimethylamino (DMABE) derivatives. The theoretical methodology employed in this study has been described elsewhere [6,7]. For each of the molecular systems, two geometries were considered, namely the ground state geometry, optimized within the Hartree–Fock (HF) approximation, and the equilibrium geometry of the CT state, optimized with the aid of the configuration interaction scheme with single excitations from the HF reference (CIS). In this step of the calculations, the modest split valence gaussian basis set 3-21G [8] was

---

* Corresponding author.

PII S1010-6030(96)04603-5

Table 1
CASPT2/DZP energies (eV) of the lowest excited singlet states of BE, ABE and DMABE calculated relative to the ground state

Molecule	$S_1(B_2)$ [a]	$S_2(A_1)$ [a]	CT(A″) [b]	S_0 [b]	$E(S_1)$ [a] − E(CT) [b]	E(CT) [b] − $E(S_0)$ [b]
BE	4.60	6.39	4.23	1.05	0.37	3.18
ABE	4.18	4.98	3.77	1.06	0.41	2.71
DMABE	4.07	4.55	3.67	1.06	0.40	2.61

[a] Calculated at the ground state geometry.
[b] Calculated at the CT state geometry.

Table 2
CASSCF/DZP dipole moments (D) of the lowest excited singlet states of BE, ABE and DMABE

Molecule	$\mu(S_1)$ [a]	$\mu(S_2)$ [a]	μ(CT) [b]	$\mu(S_0)$ [b]	$\mu(S_1)$ [a] − μ(CT) [b]	μ(CT) [b] − $\mu(S_0)$ [b]
BE	0.53	3.96	2.86	0.51	2.33	2.35
ABE	2.25	8.56	7.28	2.46	5.03	4.82
DMABE	2.90	9.50	8.68	2.80	5.78	5.88

[a] Calculated at the ground state geometry.
[b] Calculated at the CT state geometry.

employed. The geometry optimizations were performed with the GAUSSIAN program package [9]. In the second stage, the complete active space self-consistent field (CASSCF) method [10] was used to calculate the energy and dipole moments of several electronic states at a given geometry. The active space includes all π orbitals, eight for BE and nine for ABE. In the case of DMABE, the two lowest π orbitals were inactive in order to keep the number of configurations within a tractable limit. The π orbital active space was augmented by two σ orbitals (one bonding and one antibonding), both π_y (in plane) in nature, and essentially localized on the ethyne group. The double-zeta gaussian basis set of Dunning and Hay [11] with polarization functions on all atoms, except the hydrogens of the methyl groups (DZP), was used in energy and dipole moment calculations. The remaining electron correlation effects were added in the final stage with the use of multiconfigurational second-order perturbation theory, taking the CASSCF function as the reference (CASPT2) [12]. The CASSCF/CASPT2 calculations were performed with the MOLCAS3 program package [13].

All considered systems were found to be essentially planar in their ground state and CT state optimized geometries at the HF and CIS levels of approximation respectively. The geometric parameters were very similar to those already published for DMABE [7], and are therefore not presented here. The CASPT2 energies and the CASSCF dipole moments calculated for several low-lying singlet states at the two geometries are collected in Table 1 and Table 2 respectively. Energy diagrams are presented schematically in Fig. 1.

Let us first discuss the results obtained at the ground state optimized geometries. The electronic state energies calculated at this geometry represent the energies of vertical (Franck–Condon) excitation from the ground state. The two lowest excited singlet states (of B_2 and A_1 symmetry respectively in the C_{2v} point group) are dominated by $\pi\pi^*$ electronic configurations and correlate orbitally with the excited states of benzene (L_b and L_a respectively in Platt's notation).

Similar to the series of amino derivatives of benzonitrile [6], the energy of the S_1 state depends only weakly on the amino substitution, whereas the second singlet state is significantly stabilized on going from BE to DMABE (Table 1 and Fig. 1). The only experimental energy known to us is the energy of the 0–0 line determined for BE by jet spectroscopy (4.45 eV) [14]. The position of this line is indicated in Fig. 1, and it can be seen that the energy of "vertical" excitation calculated for this molecule (4.60 eV) fits reasonably well with this result. Referring to the results of Ref. [6] where such a comparison was possible for the whole series of aminobenzonitriles, and relying on the fact that the systems studied in this work are isoelectronic with the corresponding members of the aminobenzonitrile series, we can safely expect a similar precision of the present results. In analogy with the aminobenzonitriles, the dipole moments of the

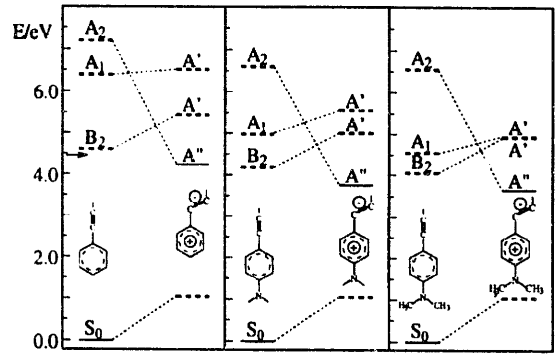

Fig. 1. The CASPT2/DZP computed energy level schemes of BE, ABE and DMABE calculated at the ground state and at the CT state optimized geometries. Energies calculated at the optimized geometry of the given state are denoted by full lines, whereas those calculated at the geometries optimized either in the ground or CT state are denoted by broken lines. Adiabatic correlations between the singlet states of a given symmetry are indicated by broken lines.

locally excited S_1 states of the aminobenzethyno series are close to those of their ground states, while the CT states are significantly more polar (Table 2). Generally, however, the aminobenzethynes are less polar than the respective members of the aminobenzonitrile series studied in Ref. [6].

The lowest excited singlet state of A_2 symmetry (which is relevant for further discussion) is located at much higher energy (6.0 eV or less) at the ground state geometry than the S_1 and S_2 states and is forbidden by symmetry for absorption from the ground state. In fact, there are two close-lying singlet states of this symmetry. They result from the $\sigma\pi^*$ and $\pi\sigma^*$ electronic configurations respectively. These states cannot easily be separated from each other due to their close proximity. In fact, their ordering and dipole moments depend on the theoretical scheme used in the calculations (single state or state-averaged CASSCF). Therefore we do not include the corresponding data in Table 1 and Table 2. Their energetic positions are, however, marked in Fig. 1. Generally, within the pair of A_2 singlet states, one state is highly polar (dominated by the $\pi\sigma^*$ configuration) while the other, dominated by the $\sigma\pi^*$ configuration, has a significantly smaller dipole moment (see Ref. [6] for a comparison). A precise characterization of these states at the ground state geometry is of minor importance, since they are not directly involved in the photophysics of these systems, which occurs on the adiabatic potential energy surface at an energy close to the bottom of the S_1 state. The only important fact is that they, or at least one of them, correlate adiabatically with the CT state as indicated in Fig. 1. As has already been discussed in previous papers [6,7], the tremendous energetic stabilization of this state on reduction of symmetry from C_{2v} to C_s can be understood as resulting from the change in hybridization of the electron-acceptor molecular moiety (the carbon atoms of the ethyne group in this case) due to an extra charge transferred from the ring and from the amino group. This has been termed the rehybridization by intramolecular charge transfer (RICT) mechanism [7].

Let us mention in this context that a closely related effect was predicted for triatomic molecules more than 40 years ago by Walsh [15]. According to the familiar Walsh diagram, triatomic molecules of the form A–B–H, where A and B are atoms of the second row, are not stable at the linear configuration if one electron occupies the antibonding π^* orbital. Occupation of this orbital can either be caused by electronic excitation or by attachment of an electron. The best known representative of this class of molecules is HCN which bends on electronic excitation to attain a bending angle of almost 120°, while the CN bond stretches to about 1.3 Å [16]. Both values are more typical of sp^2 hybridization than sp hybridization prevailing in the ground state of this molecule. The photophysics of acetylene, which is isoelectronic with HCN, can also be discussed on the basis of the Walsh diagram, since in its lowest excited states the molecule bends (to cis or trans configuration) [17] due to the same mechanism as that operating in HCN. Acetylene also bends in its CT complexes with alkali metals due to transfer of an extra charge of 0.6–0.8 electron from the metal to the π^* CC orbital [18].

The RICT mechanism has previously been found to be relevant for CT in amino derivatives of benzonitrile [6]. There are only two quantitative differences between the two classes of compounds with respect to the RICT process. First, amino derivatives of BE are generally less polar than those of benzonitrile (see Ref. [6] and Table 2). However, it should be noted that the change in dipole moment in the RICT state with respect to the "locally excited" (LE) S_1 state is very similar for both classes of compounds. Secondly, the RICT state in BE and its derivatives is much more stable with respect to the S_1(LE) state than in the benzonitrile series. Recalling that the calculated energy of the S_1(LE) state represents the energy of vertical excitation, but not that of the relaxed S_1 state, we see on inspection of the results presented in Table 1 and Fig. 1 that the RICT process is exothermic on the adiabatic potential energy surface of the S_1 state of all systems studied in this work. This contrasts with the situation found for the amino derivatives of benzonitrile, where the process is endothermic under isolated molecule conditions.

3. Conclusions

The predicted exothermicity of the RICT process in the ABE series is very promising with respect to the observation of the photoinduced CT process under isolated molecule conditions or in non-polar solvents. The possibility of studying the CT process in isolated molecules would be very helpful with respect to the elucidation of the basic mechanism of the process.

Further theoretical work is required to determine the energy barrier which separates the LE and CT minima on the adiabatic S_1 surface of the BE series. The height of this barrier controls the accessibility of the RICT state as a function of the excess energy of the optically prepared vibronic levels of the S_1 state.

Acknowledgements

This work was supported by a binational grant from the Deutsche Forschungsgemeinschaft and the Committee for Scientific Research of Poland.

References

[1] E. Lippert, W. Lüder, F. Moll, W. Nägele, H. Boos, H. Prigge, I. Seibold-Blankenstein, Angew. Chem. 73 (1961) 695.

[2] K. Rotkiewicz, K.H. Grellmann, Z.R. Grabowski, Chem. Phys. Lett. 19 (1973) 315.

[3] Z.R. Grabowski, K. Rotkiewicz, A. Siemiarczuk, D.J. Cowley, W. Baumann, Nouv. J. Chim. 3 (1979) 443.

[4] E. Lippert, W. Rettig, V. Bonačić-Koutecký, F. Heisel, J.A. Miehé, Adv. Chem. Phys. LXVIII (1987) 1.

[5] Th. van der Haar, A. Hebecker, Y. Il'ichev, Y.-B. Jing, W. Kühnle, K. Zachariasse, Recl. Trav. Chim. Pays-Bas 114 (1995) 430.

[6] A.L. Sobolewski, W. Domcke, Chem. Phys. Lett. 250 (1996) 428.

[7] A.L. Sobolewski, W. Domcke, Chem. Phys. Lett. 259 (1996) 119.

[8] J.S. Binkley, J.A. Pople, W.J. Hehre, J. Am. Chem. Soc. 102 (1980) 939. M.S. Gordon, J.S. Binkley, J.A. Pople, W.J. Pietro, W.J. Hehre, J. Am. Chem. Soc. 104 (1982) 2797.

[9] M.J. Frisch, G.W. Trucks, M. Head-Gordon, P.M.W. Gill, M.W. Wong, J.B. Foresman, B.G. Johnson, H.B. Schlegel, M.A. Robb, E.S. Replogie, R. Comperts, J.L. Andres, K. Raghavachari, J.S. Binkley, C. Gonzalez, R.L. Martin, D.J. Fox, D.J. DeFrees, J. Baker, J.J. Steward, J.A. Pople, GAUSSIAN 92, Revision C, Gaussian Inc., Pittsburg, PA, 1992.

[10] B.O. Roos, Adv. Quantum Chem. 69 (1987) 399.

[11] T.H. Dunning, P.J. Hay, in: H.F. Schaefer III (Ed.), Methods of Electronic Structure Theory, Plenum, New York 1977.

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

[13] K. Andersson, M.R.A. Blomberg, M.P. Fülscher, V. Kellö, R. Lindh, P.-Å. Malmqvist, J. Noga, J. Olsen, B.O. Roos, A.J. Sadlej, P.E.M. Siegbahn, M. Urban, P.-O. Widmark, MOLCAS Version 3, User's Guide, University of Lund, Sweden, 1994.

[14] D.E. Powers, J.B. Hopkins, R.E. Smalley, J. Chem. Phys. 74 (1981) 5971.

[15] A.D. Walsh, J. Chem. Soc. (1953) 228.

[16] V. Marudarajan, S. Scheiner, Chem. Phys. Lett. 186 (1991) 356. B. Gazdy, D.G. Musaev, J.M. Bowman, K. Morokuma, Chem. Phys. Lett. 237 (1995) 27.

[17] D. Demoulin, Chem. Phys. 11 (1975) 329. R.E. Bandy, C. Lakshminarayan, T.S. Zwier, J. Phys. Chem. 96 (1992) 5337. J.F. Stanton, C.-M. Huang, P.G. Szalay, J. Chem. Phys. 101 (1994) 356.

[18] L.A. Erikson, J. Wang, R.J. Boyd, Chem. Phys. Lett. 235 (1995) 422.