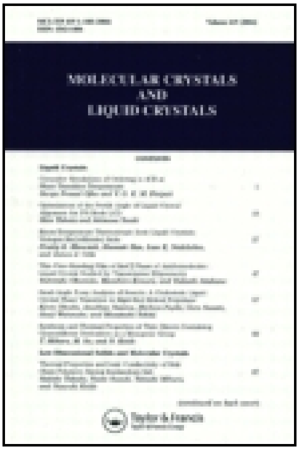

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

A Molecular Switch Involving Large Conformational Changes. A Theoretical Study

P. Sommer-larsen [a] , T. Bjørnholm [a] , M. JøRgensen [a] , K. Lerstrup [a] , P. Frederiksen [a] , K. Schaumburg [a] , K. Brunfeldt [a] , K. Bechgaard [a] , S. Roth [b] , J. Poplawski [b] , H. Byrne [b] , J. Anders [b] , L. Eriksson [c] , R. Wilbrandt [d] & J. Frederiksen [d]

[a] Centre for Interdisciplinary Studies of Molecular Interactions, University of Copenhagen, Blegdamsvej 21, DK-2100, Copenhagen ø, Denmark

[b] Max-Planck-Institut für Festkörperforschung, Heisenbergstr. 1, D-7000, Stuttgart, 80, Germany

[c] Department of Quantum Chemistry, Uppsala University, Box 518, S-751, 20, Uppsala, Sweden

[d] Department of Environmental Science and Technology, Risø National Laboratory, DK-4000, Roskilde, Denmark

Version of record first published: 04 Oct 2006.

To cite this article: P. Sommer-larsen , T. Bjørnholm , M. JøRgensen , K. Lerstrup , P. Frederiksen , K. Schaumburg , K. Brunfeldt , K. Bechgaard , S. Roth , J. Poplawski , H. Byrne , J. Anders , L. Eriksson , R. Wilbrandt & J. Frederiksen (1993): A Molecular Switch Involving Large Conformational Changes. A Theoretical Study, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 234:1, 89-96

To link to this article: http://dx.doi.org/10.1080/10587259308042901

Mol. Cryst. Liq. Cryst. 1993, Vol. 234, pp. 89–96
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Printed in the United States of America

A MOLECULAR SWITCH INVOLVING LARGE CONFORMATIONAL CHANGES. A THEORETICAL STUDY

P. SOMMER-LARSEN, T. BJØRNHOLM, M. JØRGENSEN,
K. LERSTRUP, P. FREDERIKSEN, K. SCHAUMBURG,
K. BRUNFELDT, K. BECHGAARD
Centre for Interdisciplinary Studies of Molecular Interactions, University of Copenhagen, Blegdamsvej 21, DK-2100 Copenhagen Ø, Denmark

S. ROTH, J. POPLAWSKI, H. BYRNE, J. ANDERS
Max-Planck-Institut für Festkörperforschung, Heisenbergstr. 1, D-7000 Stuttgart 80, Germany

L. ERIKSSON
Department of Quantum Chemistry, Uppsala University, Box 518, S-751 20 Uppsala, Sweden

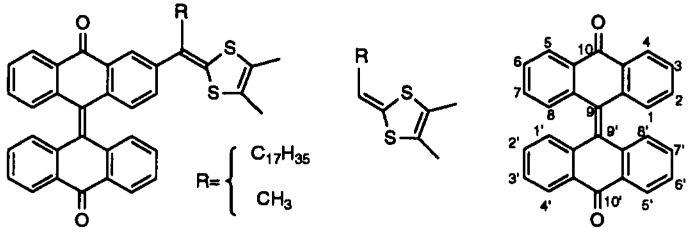
R. WILBRANDT, J. FREDERIKSEN
Department of Environmental Science and Technology, Risø National Laboratory, DK-4000 Roskilde, Denmark

Abstract *Ab initio* and semi-empirical calculations on a supramolecular structure consisting of the electron acceptor molecule bianthrone covalently linked to the electron donor molecule 2,3-dimethyl-6-alkyl-1,4-dithiafulven are prensented. The molecule may act as a molecular switch and calculations show that a charge transfer state is involved in the initial stage of the switch process. The charge recombination process is calculated to occur early in the switching process. Experimental data supports this interpretation and calculations are used as a guideline for synthetic strategies leading to molecules with improved switching properties.

INTRODUCTION

A number of experimental investigations show that the molecule bianthrone undegoes a conformational change when influenced by either light,[1-9] heat,[1-9] electrons[10-15] or under pressure.[5,6,16] We have utilized this property to design a new molecular structure which may act as a molecular switch by attaching an electron donor molecule to the bianthrone electron acceptor. The experimental data for the system and the detailed conceptual background have been described elsewhere.[17] In this paper we describe the quantum chemical calculations, which have been performed in parallel with the experimental investigations.

Fig. 1 shows the combined donor-acceptor molecule 3-(2,3-dimethyl-6-alkyl-1,4-dithiafulven-6-yl)-bianthrone (1), which consists of the electron donor molecule 2,3-dimethyl-6-alkyl-1,4-dithiafulven (2) linked to the electron acceptor bianthrone (3). The electron donor is attached with a conjugated link to the bianthrone molecule. This allows for a charge transfer (CT) state where an electron is transferred from the donor to the bianthrone acceptor. The optical CT-transition is clearly visible in the electronic spectrum of (1).[17]



(1) (2) (3)

FIGURE 1. Structures of molecules.

The conformational change during the switching between the so called A-form and B-form of bianthrone is illustrated in fig. 2 for the molecule (1).[18] The A-form of bianthrone is described as puckered and it is the stable form of neutral bianthrone.[19] The bond between the central 9,9' carbon atoms is a full double bond and each of the anthrone halfs is puckered. The B-form is a meta stable conformation of the neutral molecule reached by applying either heat, light or pressure to the molecule,[20] and it is the stable conformation of the bianthrone anion.[12] In the B-form each anthrone half is planar, and the two halfs are twisted with respect to each other around the central 9,9' bond.

The stability of the two forms is a balance between the bonding character of the central double bond, the resonance energy within each anthrone half and the steric repulsion between the anthrone halfs.

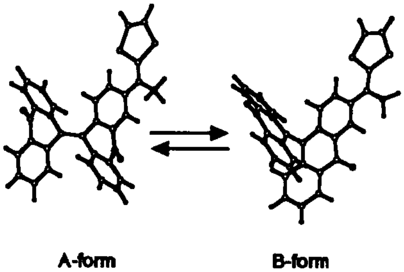


FIGURE 2. Conformational changes in (1). Optimized geometries.

The final state to which the molecule(1) switches upon absorption of light is the ground state with bianthrone in its B-form.[17] The electronic absorption spectra of the initial and final states show the two lowest transitions to be strongly influenced by the switching process.[17] In the initial state of the molecule, the two lowest transitions are at 390 nm and 475 nm, whereas they are shifted to 650 nm and 850 nm in the final state.[17]

The switching process in the system was originally expected to proceed from the initial ground state with bianthrone in its A-form over the CT-state reached by direct excitation in the CT-band, still with bianthrone in its A-form, to the CT-state with bianthrone in its B-form. This state was supposed to be stabilized by the conformational change in the reduced bianthrone part. The experimental evidence, however, shows no sign of a stabilized CT-state.

The quantum chemical calculations have been performed in order to understand and assign the experimental results and to describe the electronic states and potential surfaces which form the foundation of the switching process.

RESULTS AND DISCUSSION

The calculations have been performed using the Gaussian 90 and 92 programs[21] and the semi-empirical MOPAC 6.0 program.[22] All semi-empirical calculations have been performed with the PM3 method,[23] and all *ab initio* calculations used a 6-31G basis.

Electronic properties of the donor-acceptor molecule (1)

No experimental evidence shows that the CT-state with bianthrone in its B-form appears during the switch process of (1). Fig. 3 suggests an explanation for this. Here the molecular orbitals of the A-form and the B-form of (1) are sketched.

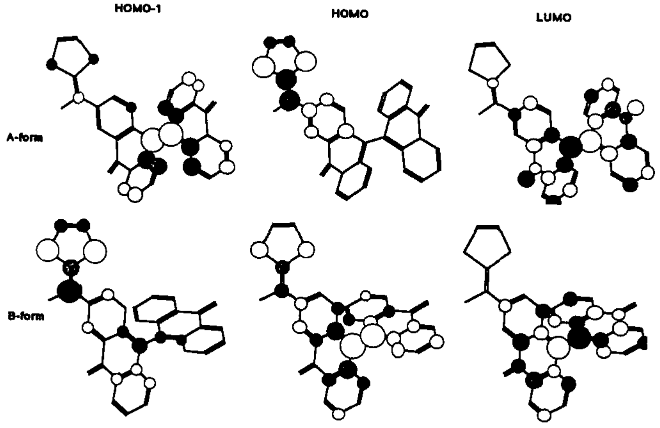


FIGURE 3. Molecular orbitals for the A- and B-forms of (1).

The molecular orbitals results from *ab initio* calculations, and they are mostly of π-character in the planar parts of the molecule. An open circle indicates a positive phase and a dashed circle indicates a negative phase of the π-like parts of the molecular orbitals. The calculations have been performed in a geometry, where the donor is coplanar with the part of the acceptor to which it is attached. The geometry has been optimized with the PM3 method. As it can be seen, the lowest unoccupied molecular orbital (LUMO) is similar in the A- and B-forms, whereas the highest and second highest occupied molecular orbitals (HOMO and HOMO-1) are interchanged in the A- and B-forms. This results in the interchange of the CT-state and an excited state localized on bianthrone, when the conformation changes from the A-form to the B-form. The switch process is initiated in the A-form CT-state. As a consequence of the interchange of levels, the system will cross over from the potential curve of the CT-state to the potential curve of the localized bianthrone state before the minimum in the CT-state potential curve at the B-form conformation is reached. Hence, the attachment of the donor to bianthrone influences the initial stage of the switch process, whereas the finial stage should behave as in bianthrone itself. The experimental results seems to confirm this interpretation.[17]

The absorption band at 390 nm in the A-form of (1) is assigned to the local bianthrone excitation and the 475 nm band to the CT excitation.[17] According to the calculated molecular orbitals, the lowest excited state in the B-form (850 nm) corresponds to a mostly local excitation and the 650 band corresponds to a partial CT-excitation. Fig. 4 shows an orbital diagram in which the experimental transitions is indicated. The occupied levels are the energies from the *ab initio* calculation. The LUMO levels are the negative vertical electron affinities (EA) calculated with the semi-empirical method. Due to orbital relaxation, this gives a more correct picture of the excitation in a simple orbital diagram. The mixing of the donor HOMO and the bianthrone HOMO in the B-form, which also appears from fig. 3, results in a raise of the HOMO level for (1) in the B-form and a lowering of the HOMO-1 level. The raising of the HOMO level of the B-form with respect to that of the A-form has been experimentally verified. The experimental difference in oxidation potentials between the A-form and the B-form is 0.18 eV[17], whereas the calculated difference in Koopmans ionization potentials is 0.65 eV.

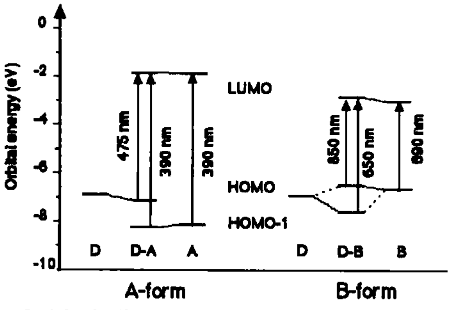


FIGURE 4. Orbital diagram. D: Donor levels. A,B: Levels for the A- and B-forms of bianthrone. D-A,D-B: Levels for the A- and B-forms of (1).

The splitting of the HOMO and HOMO-1 levels of the B-form is also the origin of the shift of the lowest (850 nm) and second lowest (650 nm) transition in the absorption spectrum towards respectively longer and shorter wavelengths compared to the absorption in the bianthrone B-form itself at 690 nm[4a], see fig. 4.

The correct description of the excited states of the B-form is obviously more complicated than a simple HOMO->LUMO transition as the molecule has a partly biradical character. In the biradical situation, both double excitations in the HOMO to LUMO manifold and excitations on each anthrone half are important. These excitations introduce two more unoccupied levels, hence at least a multi configuration self consistent field (MCSCF) calculation in the HOMO-1 to LUMO+2 manifold is necessary in order to describe the excited states in the B-form correctly.

The above analysis indicates a way to optimize the molecule (1) so that the switch process follows the original imagined route as discussed in the introduction. In order to avoid the crossing between the potential curves, so that the charge transferred state continues to be the lowest excited state also in the B-form, the conclusion can be drawn based on fig. 3,4, that *this is most efficiently obtained by lowering the HOMO of the bianthrone acceptor.* From the HOMO of the B-form in fig. 4, it may be seen that this can be obtained by substituting electron withdrawing groups in the 1,1', 3,3', 6,6' and 8,8' position of bianthrone (fig. 1). As the 1 and 8 positions may influence the switching properties, only the 3 and 6 positions are open for substitution. Synthetic work following these lines are in progress.

Potential curve for rotation of the donor group

The geometric arrangement of the donor group with respect to the part of bianthrone, to which it is attached, is very important for the oscillator strength of the CT-transition.

The potential curve in fig. 5 for rotation of the donor group around the single bond, with which it is attached to bianthrone, has been calculated with the semi-empirical method. Even though it predicts a minimum at 90°'s rotation, it is important that the potential curve extends over no more than 2 Kcal/mol. This low rotational barrier is a consequence of the balance between the steric repulsion, which is minimized at 90°'s rotation, and the resonance energy, which is maximized at the coplanar conformation (0° rotation).

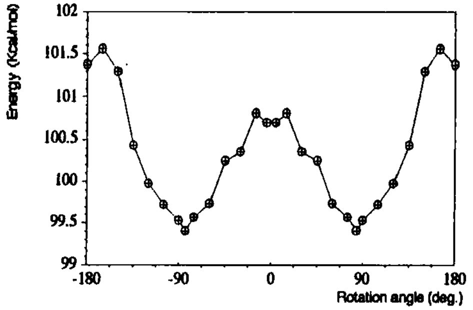


FIGURE 5. Heat of formation as a function of rotation of the donor group.

This low barrier may also exist in the excited CT-state. In that case, the geometric arrangement has a direct influence on the degree of charge transfer in the excited state. In the coplanar conformation, only a partial charge transfer occurs. The spread of electron density in the HOMO of the A-form (fig. 3) towards the acceptor results in a decrease of charge transfer in the HOMO->LUMO transition. The single HOMO->LUMO configuration in the 90°'s rotated conformation induces on the other hand a transfer of a full electron.

This has implications for the strength of the emission in polar solvents. In polar solvents, charge transfer is stabilized and a rotation of the donor molecule around the single bond connecting the donor to the acceptor will increase the charge transfer, but decrease the oscillator strength for the HOMO → LUMO transition. Experimentally it is observed that the intensity of the fluorescence strongly decreases in polar solvent even though the stabilization of the excited state is increased (the fluorescence lifetimes increase).[17]

Potential surfaces for bianthrone

The conformational changes which occur when the bianthrone molecule changes from the A-form to the B-form are mainly described by two dihedral angles - the twist angle and the puckering angle. Potential surfaces for the heat of formation as a function of these two dihedrals are shown in fig. 6 for the ground state (S_0), the first excited singlet state (S_1) and for the first triplet state (T_1). All geometrical parameters other than the two dihedrals have been optimized in the ground state at all points. The calculation was performed as a semi-empirical biradical calculation.[22]

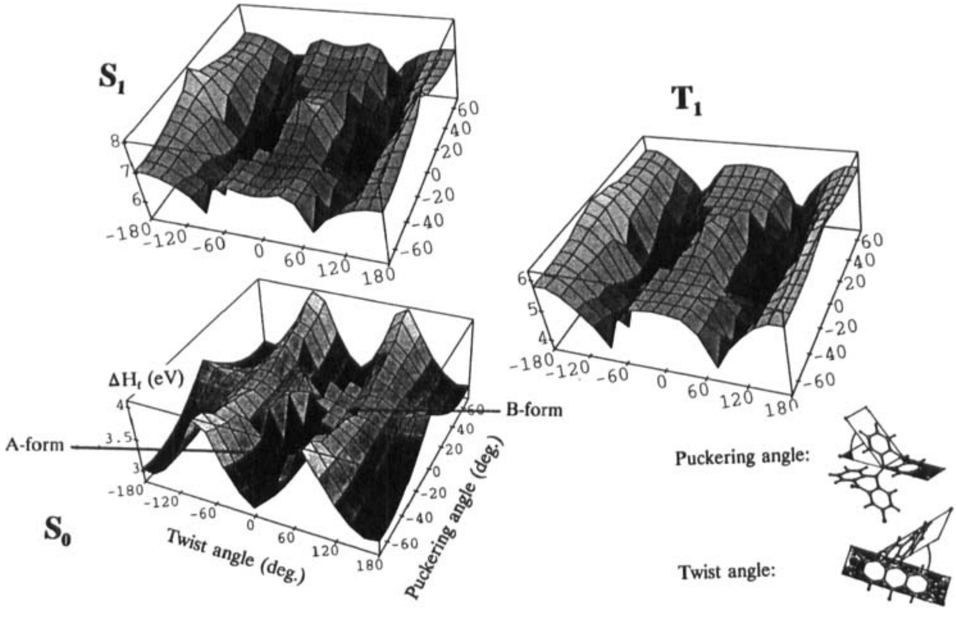


FIGURE 6. Potential curves for bianthrone. The A- and B-forms is indicated at the ground state potential curve.

The geometrical parameters and heats of formation for the A- and B-forms are similar to those found previously with similar methods.[24] The twist angle is 58° in the B-form and the puckering angle is 48° in the A-form. There exists a discrepancy between the calculated and measured enthalpy difference for the A->B conversion. The calculated value of ΔH (14 Kcal/mol) compared to the one measured in solution[25] (~3 Kcal/mol[10,25,26]) underestimates the stabilization of the B-form, whereas the activation energy for the A->B conversion (14.5 Kcal/mol) is in better agreement with the experimental value of ~18 Kcal/mol.[10,13] An *ab initio* Hartree-Fock calculation for the A- and B-forms in the geometries optimized with the PM3 method gave a similar enthalpy difference of 16.3 Kcal/mol.

The potential curve for S_0 shows that the transformation from the B-form to the A-form involves an initial puckering of the B-form. This is in disagreement with the findings in ref. 24, but it agrees with the conclusion in ref. 13.

As can be seen from the ground state potential surface, an other local minimum exists at a twist angle of 166° and a puckering angle of 62.5°. This conformation lies only 3.4 Kcal/mol higher in energy than the A-form and it is denoted the E-form.[4c] A number of metastable conformations of bianthrone exists, but only the A- and B-forms are studied in details in this paper.

The excited states surfaces all show an absolute minimum in the 90° twisted conformation. The triplet state is in fact nearly degenerate with the ground state singlet in this conformation as the molecule becomes a biradical[24].

SUMMARY

It was found that the CT excited state and an excited state localized on bianthrone are interchanged when (1) changes conformation from the A-form to the B-form. As a consequence, the CT-state with bianthrone in its B-form may never participate in the switch process.

A weak rotational barrier for rotation of the donor group was found. The geometrical arrangement of the donor is important for the degree of charge transfer and the oscillator strength in the CT-transition.

The potential surfaces for the transformation between the A- and B-forms gives information on reaction paths and conformations in the excited states.

ACKNOWLEDGEMENTS

This work was supported by the EEC ESPRIT Basic Research Actions, grant no. 3314 (MOLSWITCH), and by the Danish Materials Technological Development Programme.

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