linkages as well. The latter are obviously very weak. Interestingly, the ferromagnetic interactions in Prussian blue also occur through the N-C-Fe^{2+}-C-N closed-shell linkage.[17–19]

Experimental Section

$K_4[Mo(CN)_7] \cdot 2H_2O$[15] and $[MnL(H_2O)_2]Cl_2 \cdot 4H_2O$[14] were prepared as already described. Dark red single crystals of **1** were obtained by slow diffusion in an H-shaped tube under nitrogen of two deoxygenated 10^{-4} M aqueous solutions containing $K_4[Mo(CN)_7] \cdot 2H_2O$ and $[MnL(H_2O)_2]Cl_2 \cdot 4H_2O$, respectively.

Crystal data for **1** ($C_{113}H_{126}N_{53}O_{19.5}Mn_6Mo_3$): monoclinic, space group $C2/c$; $a = 40.30(3)$, $b = 16.942(3)$, $c = 24.464(13)$ Å; $\beta = 120.98(2)^\circ$; $V = 14319$ Å^3; $Z = 4$. Data were collected on a four-circle diffractometer Enraf-Nonius with graphite-monochromated $Mo_{K\alpha}$ radiation. A total of 13592 reflections were collected in the range $1.18 < \theta < 25.46^\circ$, and were used after a semiempirical absorption correction had been applied. The structure was solved by direct methods and refined against all F^2 data to $R1 = 0.0714$, $wR2 = 0.1425$ for 5088 reflections with $I \leq 2\sigma(I)$, GOF = 0.930. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-117388. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

The magnetic measurements were carried out with a Quantum Design MPMS-5S SQUID magnetometer working in both the dc and ac modes down to 2 K and up to 50 kOe. The diamagnetic correction was estimated as 1260×10^{-6} emu mol^{-1}.

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The Photoisomerization of *cis*-Stilbene Does Not Follow the Minimum Energy Path

Christian D. Berweger, Wilfred F. van Gunsteren,* and Florian Müller-Plathe

The development of femtosecond spectroscopy has made it possible to monitor chemical reactions in real time. As a prototype, the photoisomerization of stilbene in solvent has been examined under various conditions (temperature, pressure, solvent).[1–7] However, important issues such as the atomic detail of the reaction dynamics or the shape of the potential energy landscape still remain experimentally unresolved. Computational methods allow the detailed study of the time-resolved dynamics of these systems. Molecular dynamics[8, 9] provides the time-dependent evolution of the system and allows for effects due to temperature and solvent, whereas accurate potential energy surfaces are provided by quantum chemistry.[10] By combining the two methods,[11–14] the best from both worlds can be used: The explicit treatment of the solvent and the evolution in time by classical molecular dynamics, and the unbiased description of the reacting molecule by quantum chemistry. However, the latter is computationally rather demanding. Evaluation of potential energy and forces for photoexcited stilbene takes about half an hour on a modern microprocessor. As thousands, or rather millions of such evaluations are required for a meaningful molecular dynamics simulation, a straightforward implementation of this concept is not feasible. For this reason, we recently developed an interpolation method based on finite elements.[15, 16] The method represents the part of the potential energy surface that is required during the simulation without losing the accuracy of the quantum chemical method. This reduces the number of quantum chemical evaluations by a factor of about 2000 compared to a straightforward implementation. However, only the central dihedral angle and the two phenyl torsion angles are allowed to move for the method to be efficient. Also, the model does not include deactivation mechanisms such as fluorescence or internal conversion.

Stilbene in its first excited state is treated by a singly excited configuration interaction calculation in a 6-31G basis set. Supercritical argon is used as a model solvent at the appropriate density (2744 argon atoms with periodic boundary conditions, Lennard-Jones parameters for classical solvent–solvent and stilbene–solvent interaction from the GROMOS96 force field[9]). In total, 800 trajectories were simulated at different pressures and temperatures, at least 20 trajectories for a single state point. More computational details are given elsewhere.[16] Previous theoretical work on

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the isomerizations of stilbene generally used an empirical potential energy surface, or treated the isolated molecule.[17–20]

Figure 1 shows the potential energy surface as a representation in internal coordinates, namely the central ethylenic dihedral angle and the phenyl torsion angle. Both phenyl torsion angles behave similarly, so one of them is omitted for clarity. The trajectory of the isomerizing system is drawn as a white line. Starting point is the *cis* conformation in the upper right corner. Being a minimum in the ground state, this conformation has a relatively high potential energy in the excited state (82 kJ mol^{-1} above the *gauche* minimum). The energy difference is provided by the photoexcitation. After a rapid downhill motion, the minimum in the primary *gauche* region (central dihedral angle ≈50°, side dihedral angle ≈10°) is crossed. Then the barrier is climbed. It is located at a central dihedral angle of ≈90°. The barrier is crossed, and the system relaxes into the wide 8-shaped minimum in the *trans* region. This trajectory is representative for most barrier crossings that we observed in our study.

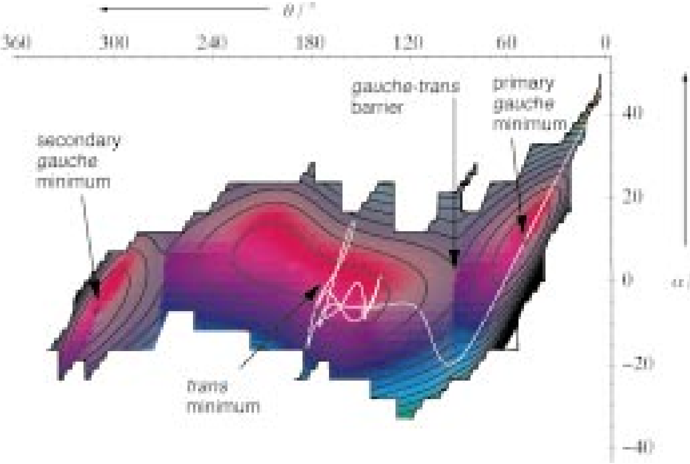

Figure 1. The potential energy surface of stilbene in its first excited state, as calculated during the simulations. An example trajectory which crosses the barrier is drawn as a white line. The contour lines are 5 kJ mol^{-1} apart. θ = central dihedral angle, α = phenyl torsion angle.

Two conclusions are drawn from the above. a) The primary *gauche* minimum is passed in one go. No relaxation takes place, and no thermal activation is required to leave it. The activation energy is provided by the kinetic energy gained from the initial downhill motion. b) The barrier is not crossed at the saddle point, which is at a position of 0° for the phenyl torsion angles and 14.2 kJ mol^{-1} above the *gauche* minimum. In fact, the average barrier crossing location is $-20°$ for both phenyl torsion angles, and the corresponding average energy is more than 19.3 kJ mol^{-1} above the saddle point. Thus, the concept of the reaction taking the "minimum energy path" is clearly not admissible. We note that in the few thermally activated events that we observed, the barrier is crossed over the saddle point *on average, but still* the average deviation from the saddle point is 7° for the phenyl torsion angles, and the energy is 4.2 kJ mol^{-1} above the saddle point.

The solvent has a profound effect on this reaction. Figure 2 shows averaged trajectories of the system at different pressures. The time evolution of the central dihedral angle and one of the phenyl torsion angles is displayed. A clear separation strictly according to pressure is obvious. Such behavior is expected, as at higher pressure the motion is quenched more effectively, and energy is dissipated to the solvent environment. The influence of the solvent is clearly visible beyond 40 fs. At low pressure, most trajectories migrate inertially to the *trans* minimum. With increasing solvent pressure, the majority of molecules is quenched before reaching the barrier, so they relax to the *gauche* minimum. This effect influences the rate constant measured by femtosecond experiments.[4] Investigations to connect this behavior quantitatively to the solvent shear viscosity are presently under way.

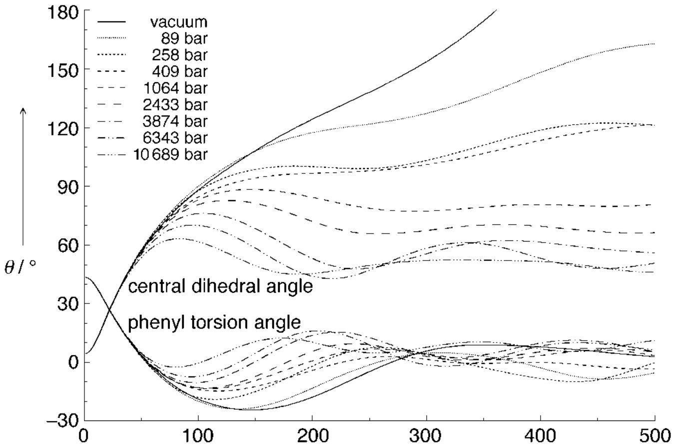

Figure 2. Averaged trajectories of the dihedral angles θ from simulations at 190 K at different pressures. All trajectories of a series of 20 simulations at the same state point, but differing in the initial solvent configurations, were averaged. t: simulation time.

It is, however, rather surprising that within the first 40 fs all trajectories coincide in spite of the fact that the environmental conditions range from vacuum over liquid to solid solvent. The solvent seems to have no effect on this short-time behavior. In the same time span, both dihedral angles change by more than 40°. However, despite the drastic change in internal coordinates, the overall shape of the molecule does not change much. Figure 3 demonstrates this by showing the initial conformation, and the conformation after 40 fs. Within this time, the two ethylenic carbon atoms and the hydrogen atoms bonded to them are displaced (Figure 3, bottom), whereas the bulky phenyl rings nearly remain in place. Thus, it is not required to move any solvent atom, and the solvent does not influence the short-time dynamics.

Our detailed analysis of the dynamics of photoexcited *cis*-stilbene shows that this reaction does not proceed by thermal activation. Rather, the excessive internal potential energy after the photoexcitation is used to overcome the barrier to the *trans*-minimum. The use of initial energy for the transition is facilitated by the fact that the first phase of the reaction can occur without large motion of the phenyl rings. There is no relaxation prior to the barrier transition, and the barrier is crossed far from the minimum energy path. Thus, the prerequisites for common concepts of reaction dynamics such

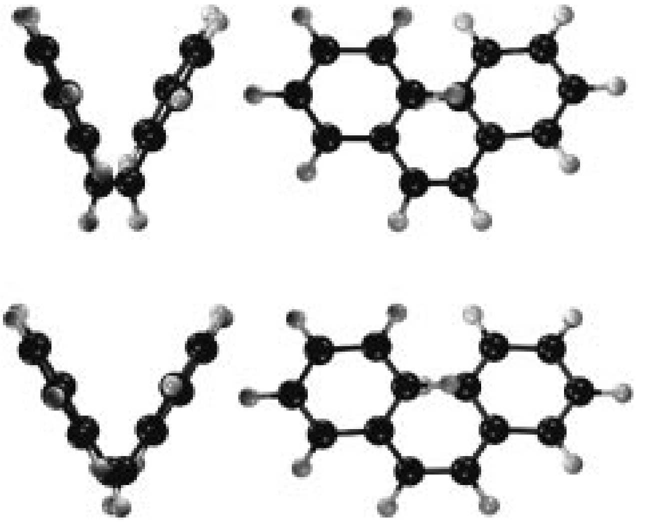

Figure 3. Initial conformation of *cis*-stilbene (top) and conformation after 40 fs of reaction (bottom). Views from the side and from the front are shown for both conformations.

as transition state theory or Rice–Ramsperger–Kassel–Marcus (RRKM) theory are not satisfied.

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