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Ab Initio Computations of Reacting Species in Crystal Lattices; Mechanistic and Exploratory Organic Photochemistry[1,2]

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Crystal lattice photochemistry quite often leads to photoproducts which differ from those obtained in solution and thus adds another dimension to organic photochemistry. In our past research we have developed quantitative methods for predicting and understanding the reaction course of a molecule entrapped in a crystal lattice.[3,4] These calculations have consisted of the following steps: (a) computationally building a "minicrystal lattice" consisting of about 20−25 molecules and just enough to have the central molecule surrounded on all sides; (b) then extracting that central molecule which is defined as the one reacting and replacing it with alternative reaction intermediates leading to alternative photoproducts, these intermediates being generated by quantum or molecular mechanics; and (c) then evaluating the energies of these alternative reacting species by molecular mechanics and the van der Waals overlap with the neighboring lattice. Both methods have been in rather good agreement with experiment. However, the weakness of such computations is the neglect of delocalization and electronic effects of the imbedded reacting species. Due to the size of even the minicrystal lattices, quantum mechanical optimization of a reacting species within a lattice has been impractical.

We have now devised an approach permitting ab initio computations on a molecule reacting in the minicrystal lattice. Our programming determines which atoms in the surrounding lattice are within a given critical distance of atoms in the reacting species and then computationally annihilates all of those lattice atoms beyond the selected distance. This stratagem, however, leaves valences "dangling" from these nearest atoms due to the severed bonds. Thus, we next replace these nearest atoms by heliums which simulate the nearest atoms that are mainly hydrogens and also which require minimal computation time. With a van der Waals radius of 1.24 Å, He provides a good approximation for hydrogen at 1.06 Å.[5] Geometry optimization of the reacting guest is carried out keeping the helium shell fixed. We also have developed the programming to replace any carbon, oxygen, and nitrogen atoms with neons. Helium replacements are most simple, but our programming permits replacement of atoms other than hydrogens by neon as well as expansion of the shell to correct for differences in van der Waals radii. However, no advantage results from these embellishments. Finally, we provide a solution to an intriguing enigma (vide infra).

Table 1. Ab Initio Energies before and after Geometry Optimization[a,b]

	before optimization		with geometry optimization	
Bicyclic **1a**:[c]				
	Endo-2,3	Exo-2,3	Endo-2,3	Exo-2,3
Cmp+Shell	-816.02712	-816.33768	-816.28448	-816.78088
Shell	-55.92535	-56.42625	-55.92535	-56.42625
Cmpd	-760.10177	-759.91143	-760.35913	-760.35463
			-1315.15087*	-2063.21176*
			- 554.78417*	-1302.84846*
			-760.36670*	-760.36330*
	Endo-3,4	Exo-3,4	Endo-3,4	Exo-3,4
Cmpd+Shell	-816.62734	-816.51405	-816.87729	-816.81137
Shell	-56.51490	-56.45517	-56.51490	-56.45517
Cmpd	-760.11244	-760.05888	-760.36239	-760.35621
5-Methyl Bicyclic **1b**:[d]				
	Endo-2,3	Exo-2,3	Endo-2,3	Exo-2,3
Cmp+Shell	-855.26003	-858.44538	-855.26722	-855.45976
Shell	-56.08549	-56.28772	-56.08549	-56.28772
Cmp	-799.17454	-799.15766	-799.18173	-799.17204
	Endo-3,4	Exo-3,4	Endo-3,4	Exo-3,4
Cmp+Shell	-855.44914	-855.38065	-855.69397	-855.65673
Shell	-56.32353	-56.48572	-56.32353	-56.48572
Cmpd	-799.12561	-798.89493	-799.37044	-799.17101
5-Ethyl Enone **5**:				
	Cis-Endo	Trans-Exo	Cis-Endo	Trans-Exo
Cmp+Shell	-894.38618	-894.64847	-894.56091	-894.71928
Shell	-55.55763	-55.68417	-55.55763	-55.68417
Cmp	-838.82855	-838.96430	-839.00328	-839.03511

[a] A 3-21G basis was employed. Energies in Hartrees (627.5 kcal/mol per Hartree). [b] Note each intermediate has different close shell atoms and thus the shells differ in energy. [c] Experimental ratio 60:40 2,3-phenol:3,4-phenol. [d] 3,4-phenol, sole product. *With C and O replaced by neons.

In this paper, we report three examples of this method. We have selected cases where the crystal lattice photochemistry differs dramatically from that in solution. The first reaction studied is the "type B bicyclic rearrangement"[6,7] of 6,6-diphenylbicyclo-[3.1.0]hexen-2-one (**1a**, R = H) which, on photolysis, is known[6,7] to afford zwitterion $\mathbf{2S_o}$. This intermediate leads onward to two phenolic photoproducts with 2,3-diphenylphenol (**3**) and 3,4-diphenylphenol (**4**) (Scheme 1). In the crystal the isomers are formed in equal quantity while in solution that 2,3-phenol **3** is predominant.

The enigma of whether it is the endo or the exo phenyl group which migrates subsequently in the zwitterion (i.e., $\mathbf{2S_o}$) to carbon-2 and carbon-4 has not been satisfactorily answered although with a *p*-cyano or a *p*-bromo substituent on one phenyl group, the endo aryl group has been shown to migrate selectively.[3a] While in principle, this question for reactant **1** could be answered by isotopic labeling, we have addressed the problem more simply computationally using the helium shell approach. Thus each of four zwitterionic species was evaluated imbedded in the crystal lattice. Scheme 1 shows the alternatives. One notes that zwitterion $\mathbf{2S_o}$ has a plane of symmetry, and one's first inclination

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(1) This is paper 184 of our photochemical series and publication 249 of our general sequence.

(2) For the previous publication of our photochemical series, see: Zimmerman, H. E. *J. Phys. Chem.* **1998**, *102*, 5616−5621.

(3) (a) Zimmerman, H. E.; Sebek, P. *J. Am. Chem. Soc.* **1997**, *97*, 3677−3690. (b) Zimmerman, H. E.; Zuraw, M. J. *J. Am. Chem. Soc.* **1989**, *111*, 2358−2361. (c) Zimmerman, H. E.; Zuraw, M. J. *J. Am. Chem. Soc.* **1989**, *111*, 7974−7989. (d) Zimmerman, H. E.; Zhu, Z. *J. Am. Chem. Soc.* **1994**, *116*, 9757−9758. (e) Zimmerman, H. E.; Zhu, Z. *J. Am. Chem. Soc.* **1995**, *117*, 5245−5262.

(4) (a) Apparently unaware of our efforts, Angermund et al. (Angermund, K; Klopp, I.; Krüger, C.; Nolte, M. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 1354−1356) have used a similar molecular mechanics method but employed product structures rather than reacting species. With kinetic control, one really needs transition structures. (b) In interesting work dealing with a rearranging carbene, Keating et al. (Keating, A. E.; Shin, S. H.; Houk, K. N.; Garcia-Garibay, M. *J. Am. Chem. Soc.* **1997**, *119*, 1474−1475) have used gas phase ab initio structures imbedded in a minilattice with energies then determined by molecular mechanics.

(5) Bondi, A. *J. Phys. Chem.* **1964**, *68*, 441−451.

(6) Zimmerman, H. E.; Grunewald, J. O. *J. Am. Chem. Soc.* **1967**, *89*, 5163−5172.

(7) (a) Zimmerman, H. E.; Nasielski, J.; Keese, R.; Swenton, J. S. *J. Am. Chem. Soc.* **1966**, *88*, 4895−4903. (b) Zimmerman, H. E.; Epling, G. A. *J. Am. Chem. Soc.* **1972**, *94*, 7806−7811.

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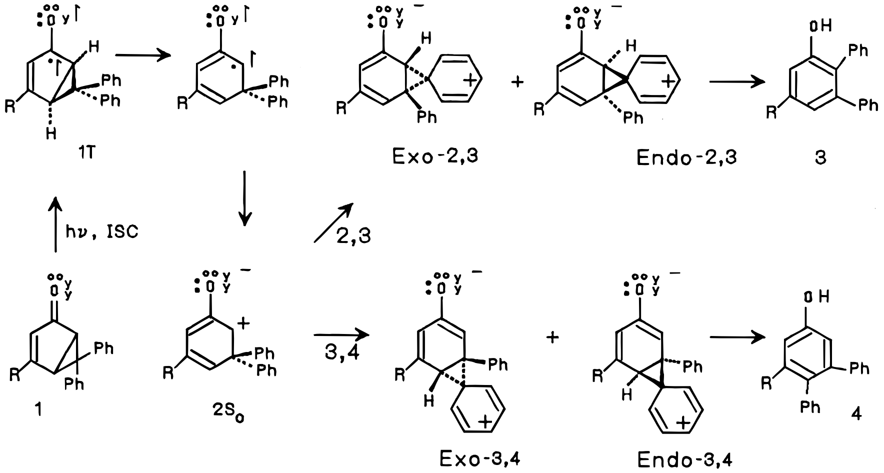
Scheme 1. The Type-B Rearrangement via **2T** and Singlet Zwitterion Intermediate **2S₀** Followed by Competitive Endo and Exo Phenyl Migrations



is to presume that the phenyl groups originally endo and exo have equal probability of migration. This is correct for solution photochemistry but not for crystal lattice photochemistry. In this case, the cavity left by the reactant 6,6-diphenylbicyclo[3.1.0]-hexene-2-one (**1**) is chiral and tends to be shaped in a way which prejudices the stereochemical course of the reactant. The upper and lower faces of the zwitterion **2S₀** are therefore non-equivalent. However, which phenyl group will migrate is, a priori, difficult to predict.[8] One can anticipate that deformation of different parts of the reacting molecule will affect delocalization and the electronic energy to differing extents. Ab initio geometry optimization takes this into account.

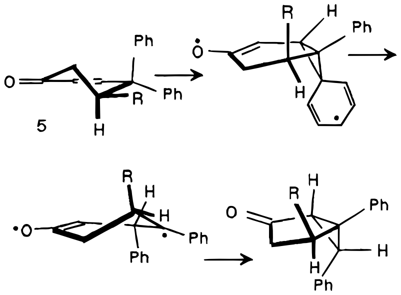
Four zwitterionic species are of interest, namely, 2,3-Endo, 3,4-Endo, 2,3-Exo, and 3,4-Exo (see Scheme 1). Ab initio computations of each of these four species imbedded in their respective helium shells show an interesting preference for the endo phenonium zwitterions. Table 1 lists the ab initio energies that were obtained.

The advantage of ab initio computations is the ability to completely include electronic effects and to take into account the excited state versus ground state nature of the intermediate involved. For excited states in general (e.g., triplets), molecular mechanics does not differentiate between these species and the corresponding ground state despite the fact that excited-state species often differ in geometry.

Similarly, computations were carried out on the substituted bicyclic **1b** (R = Me) depicted in Scheme 1. Again, the ab initio energies are given in Table 1 for the alternative reaction intermediates and predict correctly.

Additionally, computations were carried out on the type B enone rearrangement[9] (Scheme 2). The ab initio energies are included in Table 1. Here is seen that the "Trans-Exo" phenyl-bridged intermediate is preferred in agreement with experiment (i.e., sole product).

Scheme 2. Preferred Stereochemical Path for the Crystal Lattice Type B Enone Rearrangement of 5-Substituted Cyclohexenones (R = Et)



Inspection of the ab initio energies before and after geometry optimization reveals a large relaxation energy. This clearly is more than the intermediate species reorienting itself in the helium shell. Rather, groups which have been aligned to minimize van der Waals effects now conformationally twist in order to include electronic delocalization.

Finally, it needs to be noted that in the study of crystal behavior there has been emphasis on the role of stress[10] of the crystal lattice on an included molecule while our approach emphasizes alternative geometries which will fit into a rigid lattice. While both factors are, no doubt, important, our view is that the very large different shapes of competitive transition structures outweigh the role of lattice resiliency.

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[8] This phenomenon of selective aryl migration was questioned recently by a referee who commented that it looked as if the exo aryl group had more free space for motion.

[9] (a) Zimmerman, H. E.; Wilson, J. W. *J. Am. Chem. Soc.* **1964**, *86*, 4036−4042. (b) Zimmerman, H. E.; Rieke, R. D.; Scheffer, J. R. *J. Am. Chem. Soc.* **1967**, *89*, 2033−2047. (c) Zimmerman, H. E.; Kutateladze, A. G. *J. Org. Chem.* **1995**, *60*, 6008−6009.

[10] (a) McBride, J. M. *Acc. Chem. Res.* **1983**, *16*, 304−312. (b) Peachey, N. M.; Eckhardt, C. J. *J. Phys. Chem.* **1993**, *97*, 10849−10856.