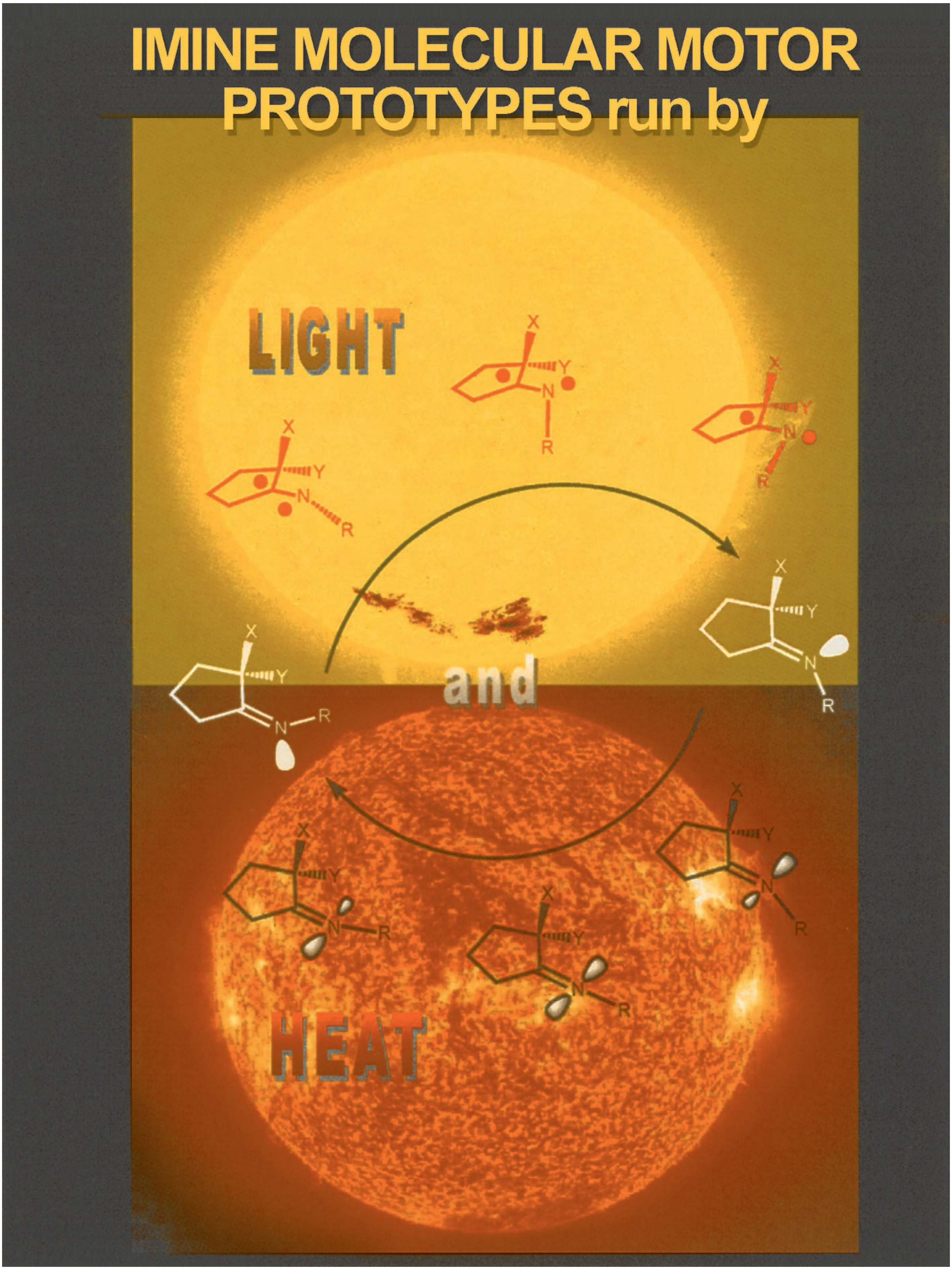
IMINE MOLECULAR MOTOR PROTOTYPES run by
LIGHT
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DOI: 10.1002/chem.200600489

Conjecture: Imines as Unidirectional Photodriven Molecular Motors—Motional and Constitutional Dynamic Devices

Jean-Marie Lehn*[a]

Abstract: Compounds containing the C=N group, such as imines and their derivatives, may undergo *syn–anti* isomerization by two different routes: 1) photochemically, by out-of-plane rotation around the carbon-nitrogen double bond through a "perpendicular" form, and 2) thermally, by in-plane nitrogen inversion through a "linear" transition state. When the two interconversions occur in sequence, a full, closed process is accomplished, restoring the initial state of the system along two different steps. In a chiral imine-type compound, for example, with an asymmetric center next to the C=N function, photoinduced rotation may be expected to occur in one sense in preference to the opposite one. Thus, photoisomerization followed by thermal isomerization in a chiral imine compound generates unidirectional molecular motion. Generally, imine-type compounds represent unidirectional molecular photomotors converting light energy into mechanical motion. As they are also able to undergo exchange of the carbonyl and amine partners, they present constitutional dynamics. Thus, imine-type compounds are double dynamic, motional, and constitutional devices.

Keywords: imines · isomerization · molecular devices · molecular motors · photochemistry

Introduction

Molecular motors play a crucial role in mechanical as well as substrate-transport processes in biology.[1] They have also been target of extensive synthetic efforts striving for the realization of organic/inorganic synthetic molecular motors[2] or motors based on biological components, such as DNA,[3] with the goal of generating directional motion by coupling directionless Brownian motion with molecular asymmetry.[4] Mechanical motions induced in particular by photochemical and electrochemical processes have been produced by using intriguing and structurally highly attractive architectures, such as catenanes and rotaxanes.[2,5]

Systems that undergo large-amplitude extension/contraction molecular motions, induced by metal-ion binding/release[6] or protonation/deprotonation[7] and fueled by acid/base neutralization, have been reported by our group.

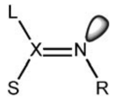
The main challenge in developing a proper molecular motor is to produce unidirectional motions, that is, motions accomplishing a full cycle by an oriented sequence of steps. This has been achieved in recent years[8] in imaginative fashion in chiral helical systems[9] and multistage catenanes[10] making use of a series of photochemical/thermal and electrochemical processes.

Imines as Unidirectional Molecular Motors

I wish to point out that there is a simple system, very easy to access, that in principle brings about light-induced, unidirectional molecular motion and thus qualifies as a proper molecular motor.

This system covers a whole class of well-known, very diverse and widely distributed compounds, of synthetic as well as biological nature; that is, principally, all unsymmetrically substituted double bonds X=N in which X is C or N, as present in imines, oximes, hydrazones, azo compounds, and so forth. The light-driven engine **1** is depicted here; L and S represent large and small substituents and R any group.

The full motional motor process is best illustrated on the basis of imines (X = C in **1**) as shown in Figure 1 and applies also to azo compounds (X = N, S = lone pair).



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[a] Prof. J.-M. Lehn
Institut de Science et d'Ingénierie Supramoléculaires
Université Louis Pasteur, 8 Allée Gaspard Monge
67000 Strasbourg (France)
Fax: (+33) 390-245-140
E-mail: lehn@isis.u-strasbg.fr

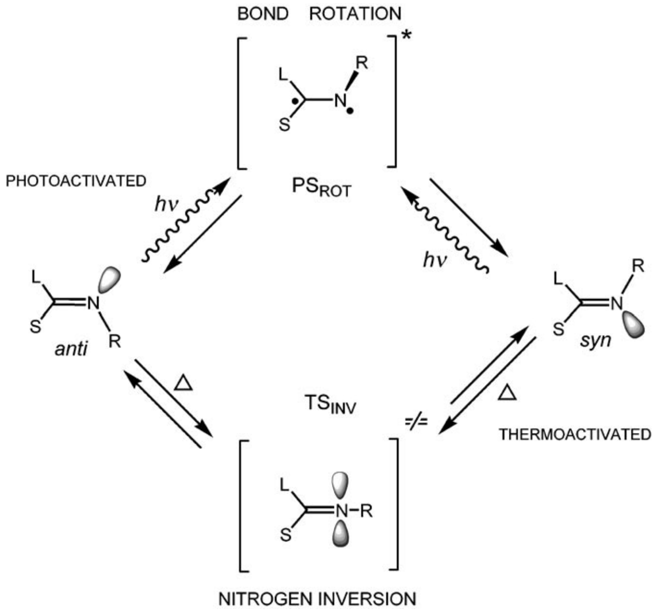


Figure 1. Representation of the two configurational *syn*/*anti* isomerization processes of imines, in the case of the imine **1**. Top: photoactivated interconversion of **1** (*anti*) and **1** (*syn*) by out-of-plane rotation around the C=N bond via a perpendicular excited state structure PS_{ROT}. Bottom: thermal interconversion of **1** (*syn*) and **1** (*anti*) by in-plane nitrogen inversion via a linear transition state TS_{INV}; L, S are two different, large and small, substituents.

Imines may undergo configurational isomerization by means of two processes, either photochemically or thermally. Irradiation of imines and their derivatives leads to configurational isomerization and may convert the thermodynamically most stable *anti* (*E*) form (R *trans* to L) to the less stable (metastable) *syn* (*Z*) form (R *cis* to L).[11] The direction and the quantum yield of the reaction as well as the generation of a given photostationary state depend on the nature of the substituents. Theoretical studies lead to the conclusion that this photoisomerization occurs by out-of-plane rotation around the C=N double bond via a perpendicular structure PS_{ROT} in the singlet or triplet excited state, akin to the well-known photoisomerization of olefins.[12] This photochemical step is followed by a return to the stable *anti* form by thermally activated in-plane nitrogen inversion via a linear transition state TS_{INV}. The energy barrier to photoinduced rotation (50–60 kcal mol^{-1}[12a,d,e]) is calculated to be significantly higher than the barrier to nitrogen inversion (28–30 kcal mol^{-1}[12a,13–15]) in C=N−R imines in which R is a hydrocarbon group.[12d,e,13] Coupling of the two modes, inversion and rotation, may occur.[12b] The schematic qualitative energy profile is shown in Figure 2.

Abstract in French: *Les composés contenant le groupe C=N, tels que les imines et leurs dérivés, peuvent effectuer une isomérisation syn/anti suivant deux chemins : 1) photochimiquement, par rotation autour de la double liaison carbone-azote passant par une forme "perpendicualaire"; 2) thermiquement, par inversion de l'azote dans le plan, passant par un état de transition "linéaire". Lorsque les deux interconversions ont lieu l'une après L'autre, un cercle complet est accompli, régénérant l'état initial en suivant deux différentes étapes. Dans une imine chirale, contenant un centre asymétrique de préférence proche de la fonction C=N, la rotation photoinduite devrait se faire plutôt dans un sens que dans l'autre. Ainsi, la photoisomérisation suivie d'isomérisation thermique d'une imine chirale génère un mouvement moléculaire unidirectionnel. De façon générale, les composés de type imine représentent des photomoteurs moléculaires unidirectionnels convertissant l'énergie lumineuse en mouvement mécanique. Comme les imines peuvent aussi échanger leurs deux partenaires, amine et composé carbonylé, elles présentent une dynamique constitutionnelle. En conséquence, les composés de type imine représentent des dispositifs moléculaires à double dynamique, à la fois de mouvement et de constitution.*

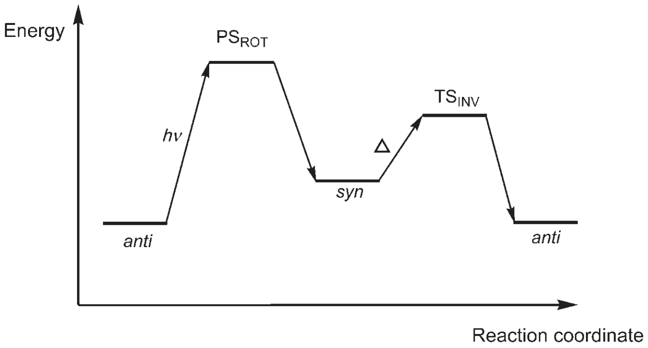
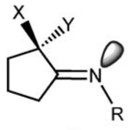


Figure 2. Schematic representation of a qualitative energy profile for configurational *syn*/*anti* isomerization of imines through photoactivated C=N bond rotation and thermally activated nitrogen inversion (see processes in Figure 1). The relative energies of the ground (*syn*/*anti*), perpendicular excited (PS_{ROT}), and linear transition (TS_{INV}) states are arbitrary.

Photoinduced rotation in **1** occurs with equal probability in a clockwise or counterclockwise fashion around the C−N axis. For the full cycling process to work as a motor and generate unidirectional molecular motion, symmetry breaking of the out-of-plane rotational motion is required, so as to obtain preferential rotation in one direction. This can be achieved by the introduction of a chiral center, an asymmetric carbon atom, optimally close to the imine group; for example, on the α-carbon as illustrated for instance by the imine **2** derived from an optically active cyclopentanone. The preference for rotation in one direction over the reverse direction defines the unidirectionality, for example, if the clockwise/counterclockwise ratio is 3:1, the overall motion compares to three steps forward/one step backward. Such imines may be considered as



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the simplest true molecular motors, representing a light-powered two-stroke engine, in which the photochemical step amounts to compression generating a high-energy state that is released in an expansion step on nitrogen inversion. The overall process is represented in Figure 3. It involves two motional steps of different symmetry character, out-of-plane rotation and in-plane inversion and breaks microscopic reversibility.

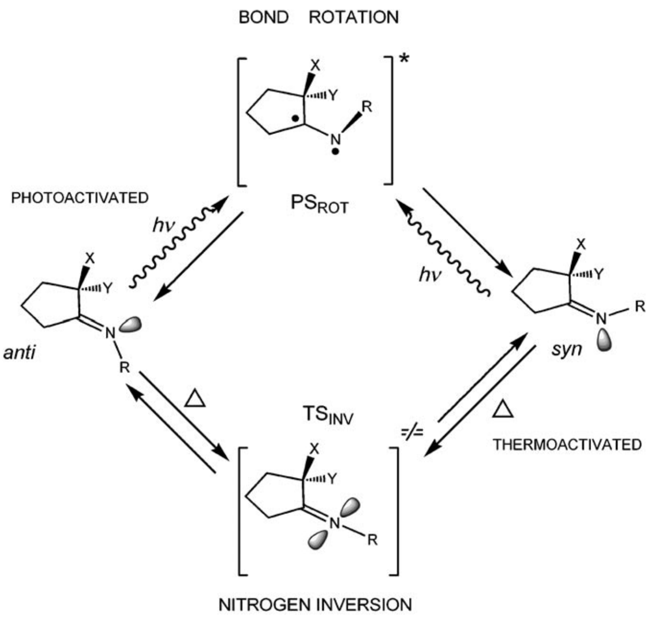

Figure 3. Configurational *syn*/*anti* isomerization in the case of the chiral imine **2**.

The relative heights of the energy barriers to C=N rotation and to nitrogen inversion may be markedly and differentially affected by structural effects. In particular nitrogen inversion rates depend strongly on the substituents on nitrogen.[14,15] Thus, the introduction of electronegative groups (such as oxygen or nitrogen) on the nitrogen center is expected to greatly increase nitrogen inversion barriers in general,[14] for instance in oximes (R = OZ),[11a,d–f,12e,16] and could well make it comparable to the rotation barrier. Conversely, push–pull disubstitution by donor (D) and acceptor (A) groups may decrease the rotation barrier in D−CX=N−A imines, possibly even below the inversion barrier. Azo-compounds −N=N− undergo photochemical *trans–cis* conversion with thermal return of the *cis* form to the more stable *trans* form.[11e,17] It is thus in principle possible to regulate the rate of cycling, that is, the speed of rotation of the motor,[9g] from very fast to very slow, through designed modification of the thermal nitrogen inversion barrier through the substituent on the C=N nitrogen atom.[14,15]

As the photoinduced rotation itself is expected to be very fast, the rate/probability of cycling will depend on the quantum yield of the reaction. Finally, as the return may in principle also occur photochemically (as is the case when a photostationary state is established), only those molecules that follow a rotation/inversion sequence undergo unidirectional motion. To this end, fast nitrogen inversion would ensure this to be the major pathway.

Imines and Two-Dimensional Chirality: Oriented Molecular Motion on a Surface

Another way to break symmetry is by deposition on a surface. The parent imine entity $CH_2{=}NH$ is chiral when confined to a plane,[18] the nitrogen site being a two-dimensional (2D) asymmetric center in two-dimensional space and nitrogen in-plane inversion representing a racemization process. These features illustrate chemistry in Flatland.[19]

Imine **1** ($X = C$) has two 2D chiral centers and is one of the two 2D diastereoisomers when $L \neq S$: nitrogen inversion corresponds to epimerization at that site. When $L \equiv S$, nitrogen inversion amounts to 2D racemization.

In azo compounds, the *anti* form has two identical 2D chiral centers and consists of two diastereoisomers, while the *syn* form is of meso type. Of course, the same holds for vicinal-disubstituted olefins XYC=CXY.

Adsorption on a surface provides the symmetry breaking required for generating unidirectional molecular motion involving out-of-plane photoinduced rotation. The unidirectionality depends on how well adsorption hinders rotation towards the surface with respect to rotation away from it. The process for imines corresponds to that illustrated in Figure 1 and its energy profile is similar (Figure 2). Such immobilization on a surface would break macroscopic reversibility.

If there is recognition between S and L, as well as between the nitrogen lone pair and R, then the deposition of a monolayer of molecules on a surface generates a homochiral, enantiomerically defined assembly in 2D space, with all molecules arranged in the same orientation so that both rotation and inversion of all would occur in the same sense.

Conclusion and Outlook: Imines as Double Dynamic Devices—Motional Dynamics and Constitutional Dynamics

Dynamic chemistry may be considered to cover three classes of processes:

1) **Reactional dynamics**: concerning the dynamic features of chemical reactions.
2) **Motional dynamics**: molecular motions of either a) external nature, overall molecular translation and reorientation, as for instance the dynamics of pyridine[20a] or benzene[20b] molecules in the pure liquids; b) internal nature, internal rotations around bonds or site inversion such as nitrogen inversion (pyramidal or planar), as well as shape changes such as helix-strand interconversion in polyheterocyclic chains;[6] c) combined external/internal

motions in the dynamics of nonrigid molecules[21] and of complex formation.[22]

3) **Constitutional dynamics**: involving changes in constitution through the exchange of the components of a supramolecular entity, due to the lability of noncovalent interactions, or of a molecular entity containing reversible covalent bonds.

1) and 2) may be considered as "classical" cases of dynamic chemistry. Constitutional dynamics define a novel aspect of dynamic chemistry of far reaching consequences on both the molecular and supramolecular levels, that is, constitutional dynamic chemistry (CDC).[23] It has been implemented on the molecular/covalent level in the recently developed dynamic combinatorial/covalent chemistry (DCC).[24,25]

Imines and related compounds may be considered to represent double dynamic molecular devices, as they display both motional dynamics, photoinduced rotation around the C=N double bond and in-plane nitrogen inversion, *and* constitutional dynamics, due to the reversibility of the C=N bond-forming reaction and the resulting ability to undergo component exchange.

As a result of exchange dynamics, constitutional dynamic diversity is generated, giving access to multiple light-driven motors potentially activated at different wavelengths through multiple photoaddressing. Note that amine exchange, by either transamination or dissociation/condensation, provides also a pathway for interconverting the *syn* and *anti* forms of imines, when nitrogen inversion is too sluggish.

In conclusion, chiral C=N compounds such as imines fulfil the criteria of molecular motors: 1) energy supply: light, 2) directionality by symmetry breaking, and 3) coupling to the thermal bath. They represent genuine two-step light-driven unidirectional molecular engines, that is, photomotors, generating no waste and converting light energy into oriented molecular mechanical motion. The motions undergone recall biological processes,[1] such as flagellar motion. Procedures may be envisaged for revealing these motions and to harness the power of the motions undergone by an array of such photomotors, ideally cycling in phase, to produce macroscopic motion.[17b,26,27]

Acknowledgements

I thank Dean Astumian and Jacques Prost for comments and discussions.

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