# Light-Driven Molecular Motors: Imines as Four-Step or Two-Step Unidirectional Rotors

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**ⓢ** *Supporting Information*

**ABSTRACT:** Chiral *N*-alkyl imines undergo unidirectional rotation induced by light and heat, thus providing a new class of molecular motors. Depending on the conformational flexibility of the stator part (the carbonyl residue) and the nitrogen inversion barrier of the rotor part (the amine residue) in the molecule, the operation mode of the motor can be controlled as either a four- or a two-step cycling motion of the rotor part.

Molecular motors play essential roles in biological processes like mechanical motion or substrate transport.[1] As a consequence, many approaches have been explored toward the design of synthetic molecular motors.[2] Directional motion can be realized by molecular asymmetry coupled to directionless Brownian motion,[3] with microscopic reversibility as the organizing principle.[4] In recent years, unidirectional molecular motion has been achieved through a sequence of steps involving various processes of chemical,[5] photochemical/thermal,[6] combined,[7] or electrical[8] nature. Especially light-driven single molecule motors, based on rotation around the C=C bond of chiral overcrowded olefins, have been shown to be capable of converting light energy into rotation of the "rotor part" with respect to the "stator part".[6] Major synthetic work for the chemical derivatization of overcrowded olefins allowed the modulation and in-depth understanding of the rotational speed,[9] within the scope of the accessibility and characteristics of C=C bonds.

Compounds containing a C=N double bond combine the features of olefinic C=C bonds with those of a nitrogen site. It was conjectured that such compounds present intrinsically the features required for a unidirectional molecular motor by virtue of the presence of two orthogonal configurational *E/Z* isomerization processes, when operating under chiral symmetry breaking: photo-induced rotation around the double bond, like in olefins, and thermally activated inversion at the nitrogen site.[10] These features render compounds like imines, oximes, or hydrazones particularly attractive as core elements of light- and heat-driven rotational molecular motors.

It is yet crucial to point out the unique thermal and photochemical properties of these structural elements. The configurational *E/Z* stability of imines is mainly dependent on the imine N-substitution, rather than on the imine C-residues.[11] The rate of the uncatalyzed *E/Z* isomerization by nitrogen inversion is spread over more than nine powers of ten. Thus, N-heteroatom derivatives (i.e., oxime ethers) have very high inversion barriers and show a marked stability, even at elevated temperature ($\Delta G^{\ddagger} > 39$ kcal/mol), followed by *N*-alkyl imines ($\Delta G^{\ddagger} > 23$ kcal/mol) and N-aryl imines as the least stable ($\Delta G^{\ddagger} < 23$ kcal/mol).[11d,12] Experimental[13] and theoretical[14] studies indicated that the thermal isomerization proceeds by in-plane nitrogen inversion, NI, (through a linear, lateral shift transition state) rather than a rotational process. The second requirement for the implementation of a C=N bond in molecular motors, the light-induced *E/Z* isomerization, was first demonstrated at low temperature.[15] Irradiation of imines converts the thermodynamically more stable to the less stable (metastable) form.[16] Theoretical studies indicated that the photochemical isomerization proceeds through out-of-plane rotation via a singlet or triplet excited state, lying significantly higher in energy (50−60 kcal/mol) than thermal inversion.[17] On the basis of the distinct trajectories in thermal and photochemical pathways, a combination of light and thermal energy on chiral imines would lead to a particularly simple and versatile realization of a molecular motor.[10] Preferred light-driven rotation in one direction stores energy, which is released by thermal nitrogen inversion.

We herein report the implementation and analyze the operation of chiral imines as molecular motors. As discussed above, the unique dynamic features of this class of compounds allow for the generation of molecular motors based on the two orthogonal modes of *E/Z* isomerization about the C=N double bond, thus expanding the realm of molecular motors by a new two-step mode of action. Concurrently, it is shown that by coupling to a further type of molecular motion, namely ring inversion (RI), a four-step rotation may be achieved, depending on the conformational ring inversion flexibility of the "stator" part in the molecule.

Diaryl-*N*-alkyl imines serve as potential candidates for our purpose, since they were described to be sufficiently stable toward thermal *E/Z* isomerization at ambient conditions.[18] In addition, they may be easily obtained in one step and on gram scale from commercial precursors. To enable unequivocal investigation of the dynamic processes, nonplanar dibenzo[*a,d*]-cycloheptene was chosen as "stator" part of the molecule. The barrier for ring inversion of the seven-membered ring depends mainly on substitution in position 1, 4, 5, and 11 (cf. **1**).[19] Condensation of commercial (*S*)-3,3-dimethyl-2-butylamine (**2a**) with dibenzo[*a,d*]cyclohepten-5-one (**1**) in the presence of TiCl₄ yielded imine **3a** in a 64:36 diastereomeric ratio (dr).

Irradiation of a sample of **3a** in CD$_3$CN with a high-pressure mercury lamp (>280 nm) for 2 h changed the dr to 45:55, as followed by $^1$H NMR. The thermal back reaction of the mixture after irradiation was observed at 25 °C, yielding the original distribution of diastereomers after 18 h (Scheme 1).

**Scheme 1. Synthesis and Light-Induced Isomerization of Imine 3**
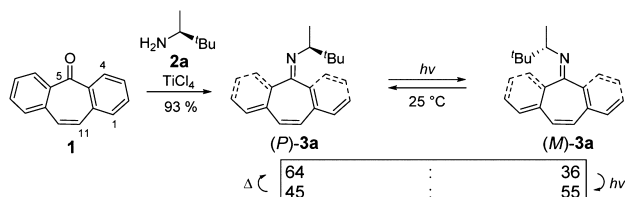


This back reaction can proceed via two pathways: (A) in-plane inversion at nitrogen (NI) or by (B) ring inversion (RI) of the cycloheptatriene moiety (Scheme 2). It is worthy to point out that both pathways are distinct from the photochemical out-of-plane rotation around the C=N bond, hence breaking microscopic reversibility.
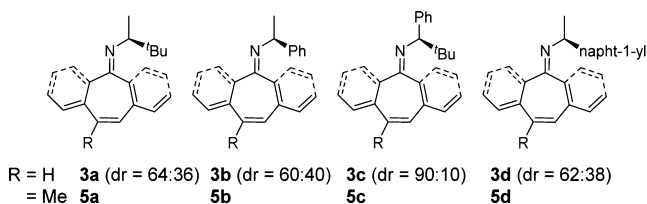
**Scheme 2. Possible Pathways for Thermal Isomerization of Imine 3**
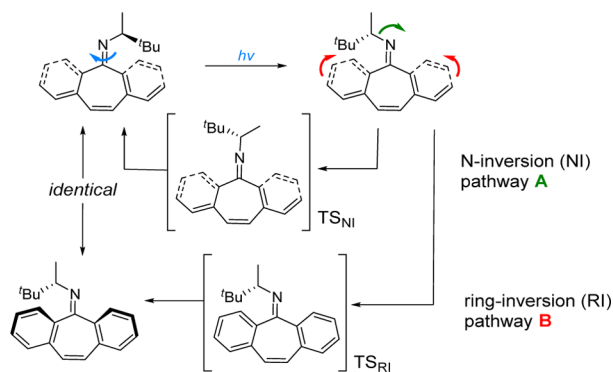


Three related imines with differing N-substituents (**3b**/**3c**/**3d**) were obtained by condensation of **1** with (S)-1-phenylethylamine (**2b**), 2,2-dimethyl-1-phenylpropan-1-amine (**2c**), or (S)-1-napht-1-ylethylamine (**2d**), in dr = 60:40 for **3b**, 90:10 for **3c**, 62:38 for **3d**. The assignment of the diastereomers was accomplished by combination of $^1$H-NOESY and $^1$H-COSY (see Supporting Information, SI). Irradiation of **3b−d** in CD$_3$CN with a high pressure Hg-lamp at 0 °C shifted the dr only slightly (<5%) because of a fast thermal re-equilibration (<5 min).

To determine the nature of the isomerization, unsymmetrical-stator derivatives (**5a−d**) were prepared by condensation of the parent ketone 10-methyl-dibenzo[a,d]cyclohepten-5-one (**4**)[20]

**Chart 1. Molecular Structures of the Imines Investigated (Only One Diastereomer Depicted)**



R = H   **3a** (dr = 64:36)   **3b** (dr = 60:40)   **3c** (dr = 90:10)   **3d** (dr = 62:38)
= Me   **5a**                  **5b**                  **5c**                  **5d**

with amines **2a−d**. Interestingly, with this stator, clear photochemical isomerization was now observed at room temperature with all imines, irrespective of the N-substitution. This behavior supported the RI pathway **B** for the fast re-equilibration with **3b−d**, since substitution at the cycloheptatriene-ring should strongly increase the energy of TS$_{RI}$ with only little affect on the barrier of the N-inversion pathway **A** (TS$_{NI}$). Fittingly, the ring inversion barrier in compounds like **3** was reported to be lower in energy (20 kcal/mol)[19e] compared to the N-inversion barrier in *N*-alkyl imines (>23 kcal/mol). In all cases, four diastereomers of imines **5a−d** were identified by NMR, according to (P)-*trans*-**5**, (P)-*cis*-**5**, (M)-*trans*-**5**, and (M)-*cis*-**5** (Scheme 3). The sample

**Scheme 3. Effect of Light and Thermal Energy on Diastereomers of Compound 5d**
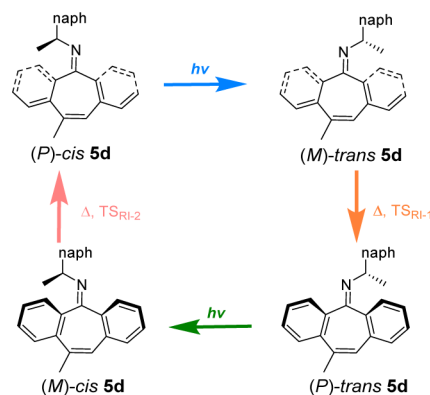


composition of the four different diastereomers could be modified by chromatographic methods, with the enrichment of specific isomers, thus allowing the investigation of their thermic and/or photochemical fate. The solid-state molecular structure of (P)-*trans* **5d** has been determined, confirming its features and providing also by extension structural information for the other related compounds (see SI, pp S20−S21).

A mixture of diastereomers **5d** consisting of 30% (P)-*cis* **5d**, 60% (P)-*trans* **5d**, 8% (M)-*trans* **5d**, and 2% (M)-*cis* **5d** was irradiated with a high-pressure Hg-lamp (>280 nm) for 1 h. The distribution of diastereomers changed substantially to 14% (P)-*cis* **5d**, 23% (P)-*trans* **5d**, 25% (M)-*trans* **5d**, and 38% (M)-*cis* **5d** (Table 1). By correlation of the differences, it could be concluded that (P)-*cis* was transformed into (M)-*trans* and (P)-*trans* was converted to (M)-cis (see Table 1 and Scheme 3).

**Table 1. Effect of Light and Thermal Energy on Diastereomer Distribution of Compound 5d (in %)**

| condition | *P-cis* | *P-trans* | *M-trans* | *M-cis* |
|---|---|---|---|---|
| start | 30 | 60 | 8 | 2 |
| 1 h irradiation | 14 | 23 | 25 | 38 |
| difference | −16 | −37 | +17 | +36 |
| 48 h at 25 °C | 28 | 29 | 20 | 23 |
| difference | +14 | +6 | −5 | −15 |

Such relationships result from the light-induced C=N bond rotation process. Storing that sample for 2 days at 25 °C led again to a significant change in distribution (28% (P)-*cis* **5d**, 29% (P)-*trans* **5d**, 20% (M)-*trans* **5d**, and 23% (M)-*cis* **5d**). As can be deduced from the relative differences, (M)-*trans* was converted to (P)-*trans* and (M)-*cis* relaxed to (P)-*cis*. From these observations it follows that molecules of type **5** indeed behave

as four-step unidirectional rotors. The rotatory motion cycle consists of alternate photoactivated energetically uphill *P/M* isomerization (via C=N bond rotation) and thermally activated ring inversion (cf. RI-pathway **B**, Scheme 2). It may be repeated at will, as was confirmed by submitting the above sample to "light and heat cycles", showing essentially the same behavior of a net directional flux (see SI).

By annealing of a benzene ring at the tricyclic core of **1**, the TS$_{RI}$ energy increases significantly to around 38 kcal/mol.[21] Consequently, the RI pathway **B** should be efficiently blocked rendering now the NI process **A** accessible (cf. Scheme 2). In this regard, imine compound **6** was synthesized. A sample with a mixture of diastereomers **6** consisting of 59% (*M*)-*cis* **6**, 11% (*M*)-*trans* **6**, 16% (*P*)-*trans* **6**, and 14% (*P*)-*cis* **6** was collected and irradiated with a TLC-lamp at 254 nm for 2 h (Scheme 4 and

**Scheme 4. Effect of Light and Thermal Energy on Diastereomers of Compound 6**
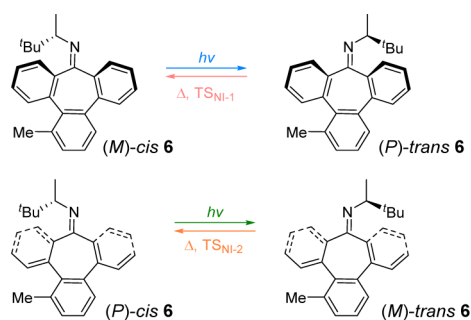


Table 2). The distribution changed to 40% (*M*)-*cis* **6**, 12% (*M*)-*trans* **6**, 35% (*P*)-*trans* **6**, and 13% (*P*)-*cis* **6**, confirming in accordance with the results from compound **5d** the conversion of (*M*)-*cis* to (*P*)-*trans* by C=N bond rotation. However, subsequent storing this sample for 2 d at 25 °C did not alter the diastereomer distribution. Only after heating to 60 °C for 15 h the composition changed, but in clear contrast to the behavior of compound **5d** (to 60% (*M*)-*cis* **6**, 11% (*M*)-*trans* **6**, 14% (*P*)-*trans* **6**, and 15% (*P*)-*cis* **6**).

As expected from the relative energies of TS$_{RI}$ and TS$_{NI}$, the N-inversion, leading from (*P*)-*trans* to (*M*)-*cis*, was now favored. Since the thermal in-plane N-inversion is of different symmetry compared to the photoactivated C=N bond rotation, this sequence also represents a molecular rotor. With respect to the four-step mode in **5d**, the displacement changes in case of **6** to a two-step mode of rotation. The initial distribution of the diastereomers is restored after heating, indicating also here the repetitive nature of the cycle, which can be repeated without fatigue.

We have herein described a novel type of unidirectional molecular motors based on imines, exploiting the specific characteristics of the C=N double bond in comparison to the C=C double bond. They present the following main features: (1) Imines are implemented here for the realization of molecular motor devices by combination of photo-induced rotation with *two* orthogonal thermal processes: NI, which is unique to imines, and RI, incorporated in the molecular framework, thus conferring triple motional dynamics to such imine-based systems; (2) by adjusting the conformational flexibility of the "stator", taking into account the thermal characteristics of the "rotor", the *mode of operation* can be either two-step (light power stroke and thermal relaxation via NI) or four-step (alternating light power stroke and thermal relaxation via RI); (3) in-plane nitrogen inversion allows for back-stroke by a *single atom* centered process; (4) the *speed* of rotation is easily controlled by independent regulation of the rates of the two orthogonal thermal processes over a wide range via the choice of the imine-*N*- and/or imine-*C*-substituent(s); and (5) the straightforward *synthetic accessibility* of imines allows for the exploration of a great variety of structural and motional features thanks to the easy preparation of a wide range of derivates, even in large quantities if needed.

Considering their remarkable features, one may note that the introduction of imines as molecular motors extends with the two-step rotation the space spanned by overcrowed olefins into a new dimension. Furthermore, in view of the possibility to exchange either component of an imine, the carbonyl or amine subunit, imine-based motors also offer the intriguing possibility to merge motional dynamics with constitutional dynamics, thus giving access in principle to motional dynamic libraries that would display a variety of molecular motors turning at different speeds. Investigations in such directions and possible applications are being pursued in our laboratory and will be reported in due course.

**Table 2. Effect of Light and Thermal Energy on Diastereomer Distribution of Compound 6 (in %)**

| condition | *M-cis* | *M-trans* | *P-trans* | *P-cis* |
|---|---|---|---|---|
| start | 59 | 11 | 16 | 14 |
| 1 h irradiation | 40 | 12 | 35 | 13 |
| difference | −19 | 1 | +19 | −1 |
| 15 h at 60 °C | 60 | 11 | 14 | 15 |
| difference | +20 | −1 | −21 | 2 |

## ■ ASSOCIATED CONTENT

**ⓢ Supporting Information**

All experimental details and analytical data. This material is available free of charge via the Internet at http://pubs.acs.org.

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**Notes**

The authors declare no competing financial interest.

## ■ ACKNOWLEDGMENTS

## ■ REFERENCES

(1) (a) Schliwa, M. *Molecular Motors*; Wiley-VCH: Weinheim, 2003. (b) Schliwa, M.; Woehlke, G. *Nature* **2003**, *422*, 759−765.

(2) (a) Balzani, V.; Credi, A.; Venturi, M. *Molecular Devices and Machines*; Wiley-VCH:Weinheim, 2008. (b) Balzani, V.; Credi, A.; Raymo, F. M.; Stoddart, J. F. *Angew. Chem., Int. Ed.* **2000**, *39*, 3348−3391. (c) *Molecular Machines, Topics in Current Chemistry*; Kelly, T. R., Ed.; Springer-Verlag: Berlin, **2005**; Vol *262*, pp 1−227. (d) Kay, E. R.; Leigh, D. A.; Zerbetto, F. *Angew. Chem., Int. Ed.* **2007**, *46*, 72−191. (e) *Molecular Switches*; Wiley-VCH: Weinheim, 2011. (f) *From Non-Covalent Assemblies to Molecular Machines*; Sauvage, J.-P., Gaspard,P., Eds; Wiley-VCH: Weinheim, 2011. (g) Coskun, A.; Banaszak, M.;

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Astumian, R. D.; Stoddart, J. F.; Grzybowski, B. A. *Chem. Soc. Rev.* **2012**, *41*, 19−30.

(3) (a) Rousselet, J.; Salome, L.; Ajdari, A.; Prost, J. *Nature* **1994**, *370*, 446−447. (b) Faucheux, L. P.; Bourdieu, L. S.; Kaplan, P. D.; Libchaber, A. J. *Phys. Rev. Lett.* **1995**, *74*, 1504−1507. (c) Jülicher, F.; Ajdari, A.; Prost, J. *Rev. Mod. Phys.* **1997**, *69*, 1269−1282. (d) Astumian, R. D.; Hängii, P. *Phys. Today* **2002**, *55*, 33−39.

(4) Astumian, R. D. *Nat. Nanotechnol.* **2012**, *7*, 684−688.

(5) (a) Kelly, T. R.; De Silva, H.; Silva, R. A. *Nature* **1999**, *401*, 150−152. (b) Kelly, T. R.; Silva, R. A.; Silva, H. D.; Jasmin, S.; Zhao, Y. *J. Am. Chem. Soc.* **2000**, *122*, 6935−6949. (c) Fletcher, S. P.; Dumur, F.; Pollard, M. M.; Feringa, B. L. *Science* **2005**, *310*, 80−82.

(6) Koumura, N.; Zijlstra, R. W. J.; van Delden, R. A.; Harada, N.; Feringa, B. L. *Nature* **1999**, *401*, 152−155.

(7) (a) Hernández, J. V.; Kay, E. R.; Leigh, D. A. *Science* **2004**, *306*, 1532−1537. (b) Leigh, D. A.; Wong, J. K. Y.; Dehez, F.; Zerbetto, F. *Nature* **2003**, *424*, 174−179. (c) Chatterjee, M. N.; Kay, E. R.; Leigh, D. A. *J. Am. Chem. Soc.* **2006**, *128*, 4058−4073.

(8) (a) Kudernac, T.; Ruangsupapichat, N.; Parschau, M.; Macia, B.; Katsonis, N.; Harutyunyan, S. R.; Ernst, K.-H.; Feringa, B. L. *Nature* **2011**, *479*, 208−211. (b) Tierney, H. L.; Murphy, C. J.; Jewell, A. D.; Baber, A. E.; Iski, E. V.; Khodaverdian, H. Y.; McGuire, A. F.; Klebanov, N.; Sykes, E. C. H. *Nat. Nanotechnol.* **2011**, *6*, 625−629.

(9) (a) Koumura, N.; Geertsema, E. M.; van Gelder, M. B.; Meetsma, A.; Feringa, B. L. *J. Am. Chem. Soc.* **2002**, *124*, 5037−5051. (b) van Delden, R. A.; Koumura, N.; Schoevaars, A.; Meetsma, A.; Feringa, B. L. *Org. Biomol. Chem.* **2003**, *1*, 33−35. (c) ter Wiel, M. K. J.; van Delden, R. A.; Meetsma, A.; Feringa, B. L. *J. Am. Chem. Soc.* **2003**, *125*, 15076−15086. (d) ter Wiel, M. K. J.; van Delden, R. A.; Meetsma, A.; Feringa, B. L. *J. Am. Chem. Soc.* **2005**, *127*, 14208−14222. (e) Pijper, D.; van Delden, R. A.; Meetsma, A.; Feringa, B. L. *J. Am. Chem. Soc.* **2005**, *127*, 17612−17613. (f) Vicario, J.; Meetsma, A.; Feringa, B. L. *Chem. Commun.* **2005**, 5910−5912. (g) Vicario, J.; Walko, M.; Meetsma, A.; Feringa, B. L. *J. Am. Chem. Soc.* **2006**, *128*, 5127−5135. (h) Klok, M.; Boyle, N.; Pryce, M. T.; Meetsma, A.; Browne, W. R.; Feringa, B. L. *J. Am. Chem. Soc.* **2008**, *130*, 10484−10485. (i) Conyard, J.; Addison, K.; Heisler, I. A.; Cnossen, A.; Browne, W. R.; Feringa, B. L.; Meech, S. R. *Nature Chem.* **2012**, *4*, 547−551. (j) Cnossen, A.; Kistemaker, J. C. M.; Kojima, T.; Feringa, B. L. *J. Org. Chem.* **2014**.

(10) Lehn, J.-M. *Chem.—Eur. J.* **2006**, *12*, 5910−5915.

(11) (a) Curtin, D. Y.; Hausser, J. W. *J. Am. Chem. Soc.* **1961**, *83*, 3474−3481. (b) Curtin, D. Y.; McCarty, C. G. *Tetrahedron Lett.* **1962**, *3*, 1269−1274. (c) Curtin, D. Y.; Grubbs, E. J.; McCarty, C. G. *J. Am. Chem. Soc.* **1966**, *88*, 2775−2786. (d) Lehn, J. M. Nitrogen inversion. In *Topics in Current Chemistry*; Springer-Verlag: Berlin, 1970; Vol. *15/3*, pp 311−377.

(12) McCarty, C. G. syn-anti Isomerizations and Rearrangements. In *Carbon−Nitrogen Double Bonds (1970)*; John Wiley & Sons, Ltd.: Hoboken, NJ, 2010; pp 363−464.

(13) (a) Reiker, A.; Kessler, H. *Tetrahedron* **1967**, *23*, 3723−3732. (b) Wurmb-Gerlich, D.; Vögtle, F.; Mannschreck, A.; Staab, H. A. *Liebigs Ann. Chem.* **1967**, *708*, 36−50. (c) Kessler, H. *Tetrahedron* **1968**, *24*, 1857−1867. (d) Kessler, H.; Leibfritz, D. *Tetrahedron Lett.* **1970**, *11*, 1423−1426. (e) Kessler, H.; Leibfritz, D. *Chem. Ber.* **1971**, *104*, 2143−2157. (f) Jennings, W. B.; Boyd, D. R. *J. Am. Chem. Soc.* **1972**, *94*, 7187−7188. (g) Kessler, H. *Tetrahedron* **1974**, *30*, 1861−1870. (h) Jennings, W. B.; Al-Showiman, S.; Boyd, D. R.; Campbell, R. M. *J. Chem. Soc., Perkin Trans.* **1976**, *2*, 1501−1506. (i) Knorr, R.; Ruhdorfer, J.; Mehlstäubl, J.; Böhrer, P.; Stephenson, D. S. *Chem. Ber.* **1993**, *126*, 747−754.

(14) (a) Lehn, J. M.; Munsch, B. *Theor. Chim. Acta* **1968**, *12*, 91−94. (b) Lehn, J. M.; Munsch, B.; Millie, P. *Theor. Chim. Acta* **1970**, *16*, 351−372. (c) Kerek, F.; Ostrogovich, G.; Simon, Z. *J. Chem. Soc. B* **1971**, 541−544. (d) Weiss, K.; Warren, C. H.; Wettermark, G. *J. Am. Chem. Soc.* **1971**, *93*, 4658−4663. (e) Jennings, W. B.; Worley, S. D. *J. Chem. Soc., Perkin Trans.* **1980**, *2*, 1512−1515. (f) Hofmann, H.-J.; Asano, T.; Cimiraglia, R. *J. Chem. Soc., Chem. Commun.* **1991**, 295−296. (g) Yamataka, H.; Ammal, S. C.; Asano, T.; Ohga, Y. *Bull. Chem. Soc. Jpn.* **2005**, *78*, 1851−1855. (h) Gálvez, J.; Guirado, A. *J. Comput. Chem.*

**2010**, *31*, 520−531. (i) He, S.; Tan, Y.; Xiao, X.; Zhu, L.; Guo, Y.; Li, M.; Tian, A.; Pu, X.; Wong, N.-B. *J. Mol. Struct.: THEOCHEM* **2010**, *951*, 7−13.

(15) Fischer, E.; Frei, Y. *J. Chem. Phys.* **1957**, *27*, 808−809.

(16) (a) van Der Linde, R.; Dornseiffen, J. W.; Veenland, J. U.; De Boer, T. J. *Spectrochim. Acta, Part A* **1969**, *25*, 375−384. (b) Yeh, H. J. C.; Ziffer, H.; Jerina, D. M.; Boyd, D. R. *J. Am. Chem. Soc.* **1973**, *95*, 2741−2743. (c) Padwa, A.; Albrecht, F. *J. Am. Chem. Soc.* **1974**, *96*, 4849−4857. (d) Padwa, A. *Chem. Rev.* **1977**, *77*, 37−68. (e) Pratt, A. C. *Chem. Soc. Rev.* **1977**, *6*, 63−81. (f) Becker, R. S.; Chagneau, F. *J. Am. Chem. Soc.* **1992**, *114*, 1373−1381. (g) Arai, T.; Furuya, Y.; Tokumaru, K. *J. Photochem. Photobiol., A* **1996**, *97*, 133−138. (h) Kawamura, Y.; Takayama, R.; Nishiuchi, M.; Tsukayama, M. *Tetrahedron Lett.* **2000**, *41*, 8101−8106. (i) Horspool, W. L. F. *CRC handbook of organic photochemistry and photobiology*; CRC Press: Boca Raton, FL, 2004, Vol. *1*.

(17) (a) Russegger, P. *Chem. Phys.* **1979**, *41*, 299−317. (b) Osamura, Y.; Yamabe, S.; Nishimoto, K. *Int. J. Quantum Chem.* **1980**, *18*, 457−462. (c) Russegger, P. *Chem. Phys. Lett.* **1980**, *69*, 362−366. (d) Bonacic-Koutecky, V.; Persico, M. *J. Am. Chem. Soc.* **1983**, *105*, 3388−3395. (e) Segawa, K.; Kikuchi, O.; Arai, T.; Tokumaru, K. *J. Mol. Struct.: THEOCHEM* **1995**, *343*, 133−140. (f) Luo, Y.; Utecht, M.; Dokić, J.; Korchak, S.; Vieth, H.-M.; Haag, R.; Saalfrank, P. *ChemPhysChem* **2011**, *12*, 2311−2321.

(18) (a) Bell, S. C.; Conklin, G. L.; Childress, S. J. *J. Am. Chem. Soc.* **1963**, *85*, 2868−2869. (b) Bell, S. C.; Conklin, G. L.; Childress, S. J. *J. Org. Chem.* **1964**, *29*, 2368−2372.

(19) (a) Conrow, K.; Howden, M. E. H.; Davis, D. *J. Am. Chem. Soc.* **1963**, *85*, 1929−1933. (b) Jensen, F. R.; Smith, L. A. *J. Am. Chem. Soc.* **1964**, *86*, 956−957. (c) Anet, F. A. L. *J. Am. Chem. Soc.* **1964**, *86*, 458−460. (d) Nogradi, M.; Ollis, W. D.; Sutherland, I. O. *J. Chem. Soc. D* **1970**, 158−160. (e) Hjelmencrantz, A.; Friberg, A.; Berg, U. *J. Chem. Soc., Perkin Trans.* **2000**, *2*, 1293−1300. (f) Tochtermann, W.; Schnabel, G.; Mannschreck, A. *Liebigs Ann. Chem.* **1967**, *705*, 169−184.

(20) Deblon, S.; Ruegger, H.; Schonberg, H.; Loss, S.; Gramlich, V.; Grutzmacher, H. *New J. Chem.* **2001**, *25*, 83−92.

(21) Tochtermann, W.; Oppenländer, K.; Walter, U. *Chem. Ber.* **1964**, *97*, 1329−1336.