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Mechanical Switching of Aromaticity and Homoaromaticity in Molecular Optical Force Sensors for Polymers

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Abstract: The sensing of mechanical stress in polymers is indispensable for investigating the origin and propagation of cracks that lead to material failure and for designing mechanically responsive polymers. Here the unique approaches of using the force-induced switching of aromaticity and homoaromaticity in molecular optical force sensors for the real time measurement of mechanical forces acting in stretched polymers are suggested. The mechanical switching of aromaticity in Dewar benzene is an irreversible event, whereas the degree of π-orbital overlap in homoaromatic compounds like homotropylium can be adjusted progressively over a wide range of forces. Using computational methods, it is demonstrated that both approaches lead to significant changes in the visible part of the UV/VIS spectra of the force sensors upon application of weak forces (pN$-$nN). Polymers that incorporate such molecular force sensors therefore change their color well before material failure occurs.

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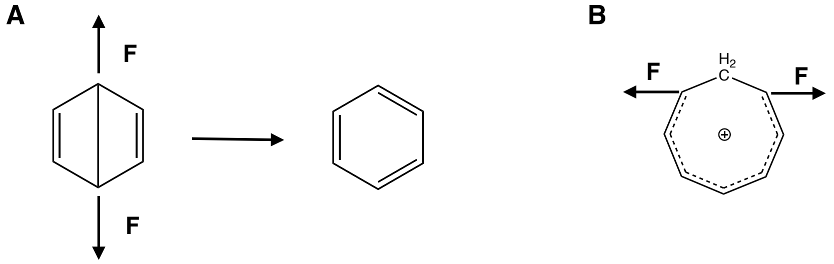
The design of stress-responsive and mechanochromic polymers has received a tremendous amount of attention during the past few years.[1,2] Recent advances in the incorporation of force-responsive units, so-called mechanophores, into the backbones of polymers[1] have allowed the synthesis of a prototypical molecular force sensor, in which the mechanically induced isomerization of spiropyran to merocyanin is accompanied by a color change of the material from yellow to red.[3] While several molecular force sensors based on changes in their vibrational,[4–6] UV/VIS,[6–8] fluorescence[9,10] or chemiluminescence[11] spectra have been reported, an ongoing challenge in the design of novel molecular force sensors is the need to generate a measurable spectral change well before material failure occurs. Using computational methods, it is here demonstrated that the mechanically induced switching of aromaticity and homoaromaticity in molecular force sensors are convenient approaches to achieve substantial changes in color at low stretching forces.

In particular, the thermodynamically stable Dewar benzene[12,13] (Scheme 1A), in which the mechanical disruption of the transannular carbon−carbon bond leads to benzene, is suggested as a force sensor. Since the electron delocalization and the π-orbital overlap of aromatic compounds are responsible for their unique spectroscopic properties, mechanical force can induce the transition from a colorless derivative of Dewar benzene to a colored derivative of benzene. It is also demonstrated that homoaromatic compounds, in which π-orbital overlap is reduced by a methylene group in the ring,[14,15] are optimal force sensors, since the degree of π-orbital overlap can be adjusted by the distance between the carbon atoms adjacent to the methylene group and hence by mechanical forces (Scheme 1B). In this paper, a derivative of the homotropylium ion that shows strong absorbance in the UV/VIS spectrum is used as a molecular force sensor.[16,17]

While mechanical switching of aromaticity has been achieved in Diels-Alder reactions,[18] to the best of my knowledge the approaches of using Dewar benzene as a molecular optical force sensor and mechanically adjusting the degree of π-orbital overlap and hence the spectroscopic properties in a homoaromatic



Scheme 1: A: Force-induced switching of Dewar benzene to benzene. B: Stretching the indicated carbon atoms in the homotropylium ion apart leads to a flattening of the molecule and to a decrease in the π-orbital overlap.

compound are unprecedented. A full account of the quantum chemical methods used in this paper can be found in the Supporting Information. It is important to note that, although the concepts of aromaticity[19] and especially homoaromaticity[15] are hard to define and widely debated, the possibilities of adjusting the π-orbital overlap in these systems by using mechanical forces proves to be very useful.

Using the quantum chemical External Force is Explicitly Included (EFEI)[20–22] method to apply forces to molecules, it is shown that the transannular carbon−carbon bond in Dewar benzene is mechanically labile. At the B3LYP[23–25]/cc-pVDZ[26] level of theory, this bond length is 1.60 Å in the dihydroxy-dinitro-derivative shown in Figure 1A. The B3LYP model was chosen because it was proven to be robust in reproducing the correct rupture forces and bond lengths in various mechanochemical pulling scenarios[2,27,28] as well as in a benchmark of spectroscopic properties relevant for this study (see Supporting Information). Applying an external force to the oxygen atoms of the hydroxyl groups, which model linkers between the molecule and a polymer backbone, leads to an increase in the transannular bond length, until rupture occurs at a force of 1.85 nN. This generates a dihydroxy-dinitro-derivative of benzene, which is itself stretched at higher forces. Although Density Functional Theory[29,30] is problematic in the case of bond rupture, it was shown that mechanochemical reactions usually remain single-reference problems until the point of bond rupture.[27] Hence, the use of DFT prior to bond rupture (and in the description of the mechanical product) is justified. It should be pointed out that the rupture force of 1.85 nN has

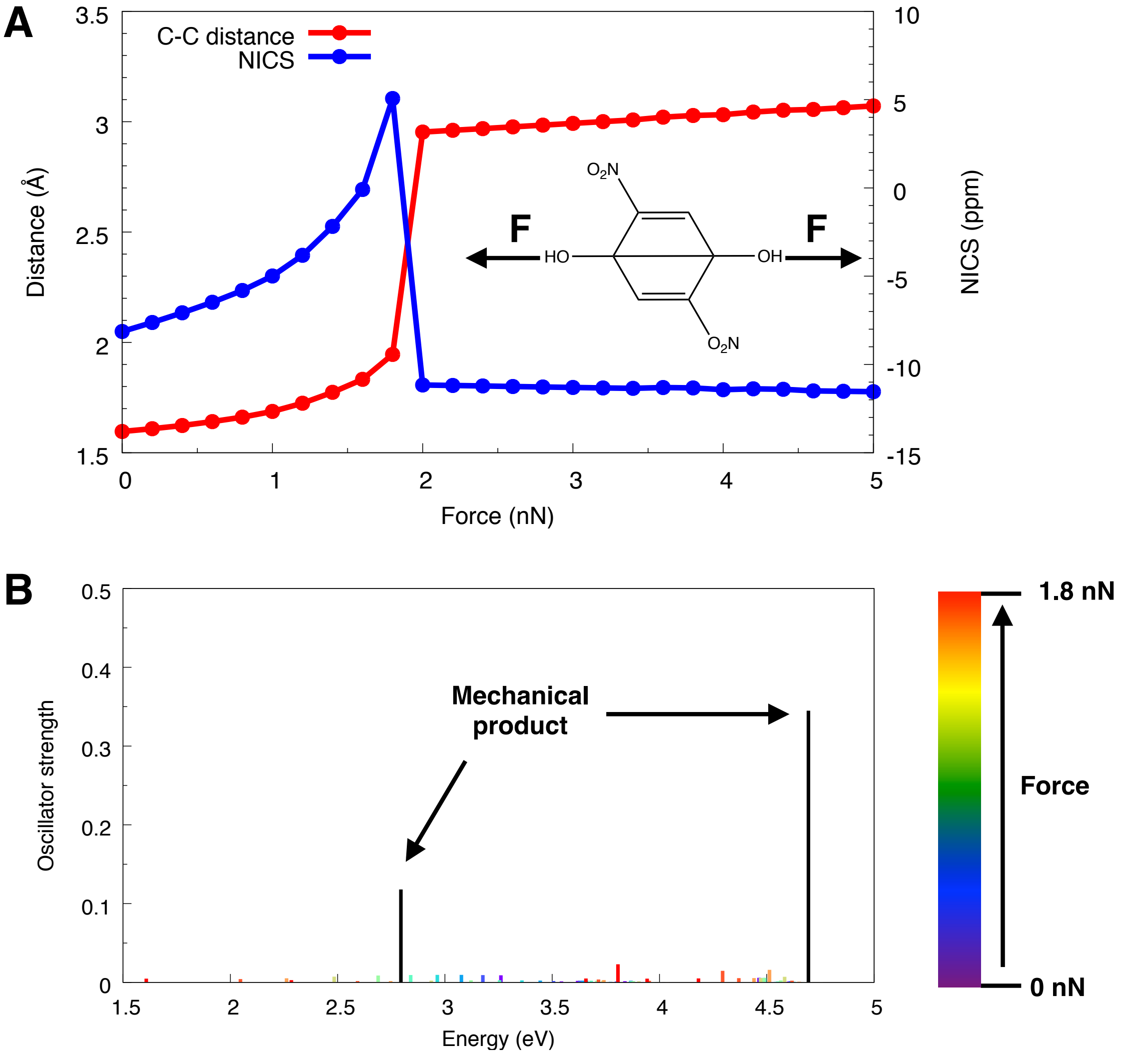


Figure 1: A: Distance between the transannular carbon atoms in a derivative of Dewar benzene (red curve) and Nucleus Independent Chemical Shift (NICS) values (blue curve) as a function of stretching force. B: UV/VIS absorption spectrum of the Dewar benzene derivative as a function of force, with each color representing a different force. The UV/VIS spectrum of the mechanical product, a dihydroxy-dinitro-derivative of benzene, is shown in black.

been determined via static quantum chemical calculations and experimental rupture forces are typically lower by a factor of 2 or 3 due to thermal oscillations.[2] Hence, experimental rupture forces of derivatives of Dewar benzene in the piconewton regime are realistic, which can at least partly be attributed to the optimal alignment of the scissile bond and the external force.

To probe the aromatic character of the molecule during this mechanochemical transformation, Nucleus Independent Chemical Shift (NICS)[31] values of the Dewar benzene derivative were calculated

(Figure 1A). In each point of the stretching coordinate, the magnetic shielding constant at the arithmetic mean of the Cartesian coordinates of the carbon atoms constituting the ring were calculated, which yields the negative of the NICS values. Strongly negative NICS values are an accepted criterion for aromaticity,[19] whereas positive values are associated with antiaromaticity. In the equilibrium geometry, the molecule is strongly bent, leading to a NICS value of -8.1 ppm at the arithmetic center of the ring due to the influence of the localized double bonds on opposite sides of the ring. Stretching Dewar benzene leads to a flattening of the molecule and to an increase in the NICS value to 5.1 ppm, thus signifying a certain antiaromatic character. Bond rupture immediately leads to NICS values around -11 ppm, which is a typical value for aromatic molecules.

From this data it can be concluded that the molecule abruptly gains aromatic character once the transannular carbon−carbon bond is ruptured. This effect has a tremendous influence on the UV/VIS spectrum (Figure 1B). In the Dewar benzene derivative, there are no low-lying electronically excited states with significant oscillator strength prior to bond rupture. Once the transannular carbon−carbon bond is broken mechanically and the molecule becomes aromatic, by contrast, intense signals in the UV/VIS spectrum can be observed. In particular, the first electronically excited singlet state (S_1) yields a strong signal at 2.79 eV (444 nm), which lies in the blue part of the electromagnetic spectrum and is a result of the unique substitution pattern. Hence, when incorporated into the backbone of polymers, appropriate derivatives of Dewar benzene can act as “binary” force sensors that yield a well-defined signal in the visible part of the UV/VIS spectrum once the transannular carbon−carbon bond is ruptured mechanically.

In contrast to Dewar benzene, the homotropylium ion does not have a bond that is predetermined for mechanical rupture. However, the methylene bridge that interrupts the CH scaffold is bent out of the molecular plane to maximize the π-orbital overlap.[14] The distance between the carbon atoms adjacent to the methylene bridge can be increased by stretching them apart mechanically (Figure 2A), which is accompanied by a planarization of the molecule and a decrease in π-orbital overlap. This leads to a decrease in aromatic character, as evidenced by the NICS values calculated throughout the stretching coordinate (Figure 2A): While the initial NICS value of -7.7 ppm is an evidence of the aromatic character in the homotropylium derivative, this value increases continuously until it passes through 0 ppm at approx. 1.8 nN. After this, the π-orbital overlap decreases more and more and the molecule becomes increasingly planar, so that the NICS values approach an asymptote at around 10 ppm, signifying antiaromaticity. Such a gain in antiaromatic character has been attributed to the methylene group providing two “pseudo” π-electrons hyperconjugatively,[32,33] resulting in 8π-electron hyperconjugative antiaromaticity.

The flattening of the molecule has a considerable influence on its UV/VIS spectrum (Figure 2B). The intense signal from the S_1 state of the molecule is located at 3.84 eV (323 nm) in the force-free state and moves rapidly to lower energies upon application of force in the pN regime. The peak moves out of the ultraviolet part of the electromagnetic spectrum and stabilizes at around 2.4 eV (517 nm), which lies in the cyan/green part of the spectrum, at a force of approx. 3 nN. Further stretching does not cause any tremendous changes in the spectrum, since the molecule is already fairly planar. This data demonstrates that homotropylium incorporated into the backbone of polymers can act as a continuous force sensor and as a “force ruler”, since, in contrast to Dewar benzene, it does not rely on a single bond rupture event to cause detectable changes in the UV/VIS spectrum, but instead the spectroscopic response is regulated continuously by the stretching force. It is noted in passing that qualitatively equivalent results are obtained for homobenzene, which is uncharged and one CH unit smaller than homotropylium (see Supporting Information).

To simulate the influence of thermal oscillations on the mechanochemical properties of Dewar benzene and homotropylium, Born-Oppenheimer Molecular Dynamics (BOMD) simulations under external forces were carried out. Derivatives of Dewar benzene and homotropylium were fitted with propyl groups that model the polymer backbone (Figure 3A). The stretching force was applied to the carbon atoms of

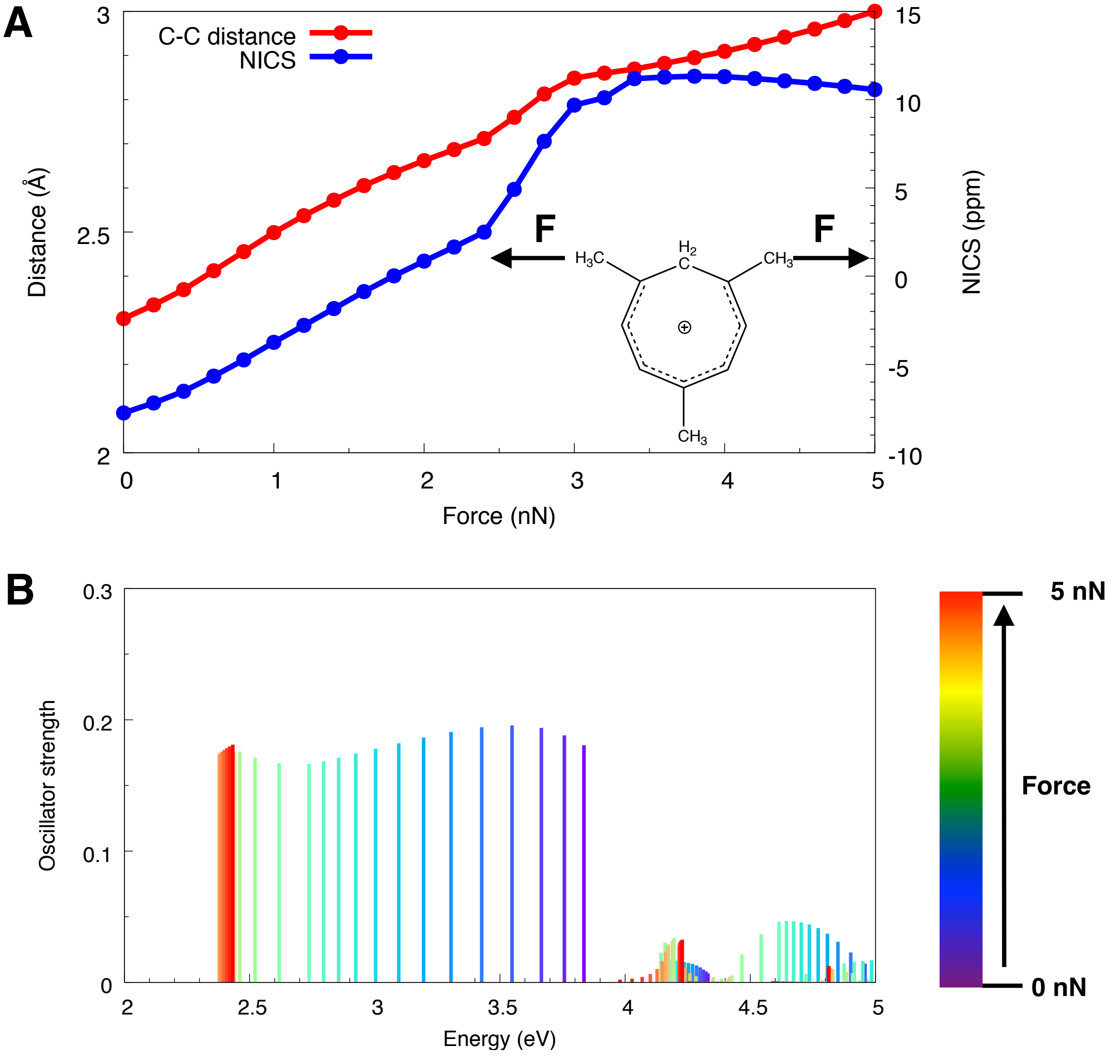


Figure 2: A: Distance between the carbon atoms adjacent to the methylene bridge in a derivative of homotropylium (red curve) and NICS values (blue curve) as a function of force stretching the carbon atoms of the methyl groups apart. B: UV/VIS absorption spectrum of the same homotropylium derivative at different stretching forces.

the terminal methyl groups and was increased by 250 pN each 96.8 fs until a total force of 5 nN was reached (see Supporting Information for further details). A total of 20 trajectories was simulated in each case.

In the case of Dewar benzene, rupture of the transannular carbon−carbon bond was observed between 1 and 1.5 ps in all trajectories. Although the applied force-loading rate is significantly higher than in an ultrasound bath, which prevents a precise determination of the rupture force observed in experiments, it can be concluded that exclusively the transannular carbon−carbon bond breaks and not one of the bonds

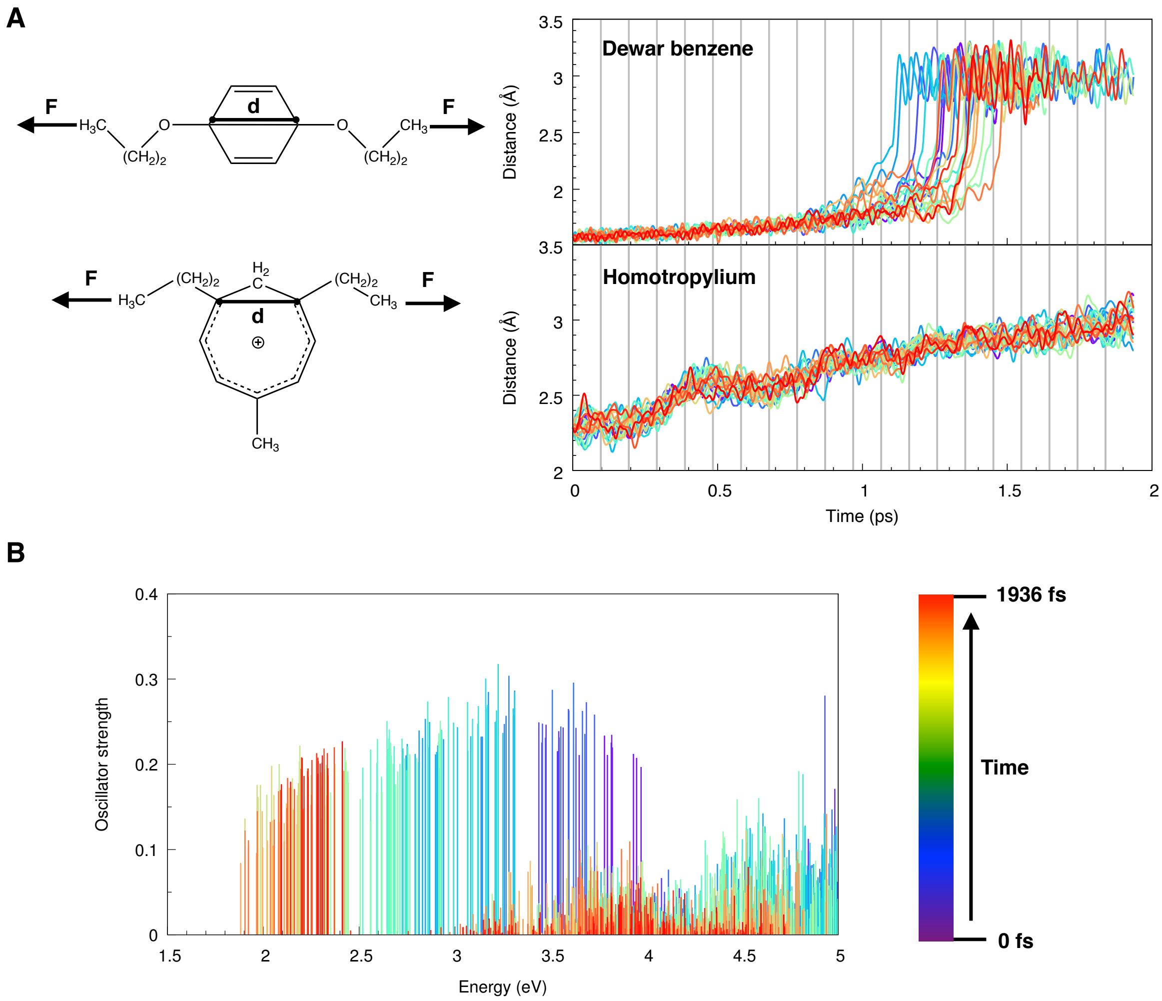


Figure 3: A: Molecular structures of the derivatives of Dewar benzene and homotropylium subjected to mechanical forces in Born-Oppenheimer Molecular Dynamics (BOMD) simulations. The progression of the distances indicated in the molecular structures are shown as a function of simulation time. Gray vertical lines in the diagrams represent those points in time when the force was increased by 250 pN. Each colored line represents a BOMD trajectory. B: Temporal evolution of the UV/VIS spectra of a representative BOMD trajectory of the homotropylium derivative.

connecting Dewar benzene to the polymer. This is an important finding, since the specific rupture of the transannular bond is a prerequisite for using the molecule as a molecular force sensor in polymers.

In contrast to Dewar benzene, the homotropylium derivative considered here shows a relatively continuous increase in bond length upon stretching in the BOMD simulation. This behavior is mirrored in the UV/VIS absorption spectra calculated along the coordinate. A representative time-dependent spectrum (Figure 3B) reveals that the peak of the S_1 state moves to lower energies with increasing simulation time (and force), as expected from the UV/VIS spectra calculated with static quantum chemical methods. Since the S_1 peak moves out of the ultraviolet into the visible region of the electromagnetic spectrum even at low forces, homotropylium holds great promise as a molecular force sensor in polymers.

Using both static and dynamic quantum chemical methods, it was demonstrated that the force-induced switching of aromaticity and homoaromaticity can lead to marked changes in the UV/VIS absorption spectra of the molecules, thus making aromatic and homoaromatic molecules ideally suited for use as molecular force sensors in polymers. Stretching Dewar benzene apart leads to an intense signal in the visible part of the UV/VIS spectrum once its transannular carbon−carbon bond is ruptured and the molecule becomes aromatic, whereas stretching the carbon atoms adjacent to the methylene bridge in homotropylium apart leads to a decrease in π-orbital overlap and to pronounced and continuous changes in the UV/VIS spectrum of the molecule even at low forces in the piconewton regime. As a result, both molecules emit visible warning signs that material failure is imminent. A future aim is to carry out calculations in the bulk in order to model the propagation of mechanical strain to the force sensors as well as their activation more realistically. It is hoped that this study triggers interest in the synthesis of polymers that incorporate aromatic and homoaromatic force sensors in their backbone.

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References

[1] A. L. Black, J. M. Lenhardt and S. L. Craig, *J. Mater. Chem.*, 2011, **21**, 1655–1663.

[2] T. Stauch and A. Dreuw, *Chem. Rev.*, 2016, **116**, 14137–14180.

[3] D. A. Davis, A. Hamilton, J. Yang, L. D. Cremar, D. van Gough, S. L. Potisek, M. T. Ong, P. V. Braun, T. J. Martínez, S. R. White, J. S. Moore and N. R. Sottos, *Nature*, 2009, **459**, 68–72.

[4] M. S. Sammon, M. Ončák and M. K. Beyer, *Beilstein J. Org. Chem.*, 2017, **13**, 1710–1716.

[5] T. Stauch, M. T. Hoffmann and A. Dreuw, *ChemPhysChem*, 2016, **17**, 1486–1492.

[6] T. Stauch and A. Dreuw, *Angew. Chem. Int. Ed.*, 2014, **53**, 2759–2761.

[7] M. J. Robb, T. A. Kim, A. J. Halmes, S. R. White, N. R. Sottos and J. S. Moore, *J. Am. Chem. Soc.*, 2016, **138**, 12328–12331.

[8] M. Á. Fernández-González, D. Rivero, C. García-Iriepa, D. Sampedro and L. M. Frutos, *J. Chem. Theory Comput.*, 2017, **13**, 727–736.

[9] S. Marawske, D. Dörr, D. Schmitz, A. Koslowski, Y. Lu, H. Ritter, W. Thiel, C. A. M. Seidel and R. Kühnemuth, *ChemPhysChem*, 2009, **10**, 2041–2048.

[10] Z. S. Kean, G. R. Gossweiler, T. B. Kouznetsova, G. B. Hewage and S. L. Craig, *Chem. Commun.*, 2015, **51**, 9157–9160.

[11] Y. Chen, A. J. H. Spiering, S. Karthikeyan, G. W. M. Peters, E. W. Meijer and R. P. Sijbesma, *Nat. Chem.*, 2012, **4**, 559–562.

[12] J. Dewar, *Proc. R. Soc. Edinb.*, 1869, **6**, 82–86.

[13] L. Ferrar, M. Mis and D. R. Robello, *Tetrahedron Lett.*, 2008, **49**, 4130–4133.

[14] S. Winstein, *J. Am. Chem. Soc.*, 1959, **81**, 6524–6525.

[15] R. V. Williams, *Chem. Rev.*, 2001, **101**, 1185–1204.

[16] R. Huisgen and J. Gasteiger, *Angew. Chem. Int. Ed.*, 1972, **11**, 1104–1105.

[17] S. Winstein, C. G. Kreiter and J. I. Brauman, *J. Am. Chem. Soc.*, 1966, **88**, 2047–2048.

[18] M. B. Larsen and A. J. Boydston, *J. Am. Chem. Soc.*, 2013, **135**, 8189–8192.

[19] A. Stanger, *Chem. Commun.*, 2009, 1939–1947.

[20] M. T. Ong, J. Leiding, H. Tao, A. M. Virshup and T. J. Martínez, *J. Am. Chem. Soc.*, 2009, **131**, 6377–6379.

[21] J. Ribas-Arino, M. Shiga and D. Marx, *Angew. Chem. Int. Ed.*, 2009, **48**, 4190–4193.

[22] K. Wolinski and J. Baker, *Mol. Phys.*, 2009, **107**, 2403–2417.

[23] A. D. Becke, *J. Chem. Phys.*, 1988, **88**, 1053–1062.

[24] C. Lee, W. Yang and R. G. Parr, *Phys. Rev. B*, 1988, **37**, 785–789.

[25] A. D. Becke, *J. Chem. Phys.*, 1993, **98**, 1372–1377.

[26] T. H. Dunning, *J. Chem. Phys.*, 1989, **90**, 1007–1023.

[27] M. F. Iozzi, T. Helgaker and E. Uggerud, *Mol. Phys.*, 2009, **107**, 2537–2546.

[28] G. S. Kedziora, S. A. Barr, R. Berry, J. C. Moller and T. D. Breitzman, *Theor. Chem. Acc.*, 2016, **135**, 79.

[29] P. Hohenberg and W. Kohn, *Phys. Rev.*, 1964, **136**, 864–871.

[30] W. Kohn and L. J. Sham, *Phys. Rev.*, 1965, **140**, 1133–1138.

[31] P. von Ragué Schleyer, C. Maerker, A. Dransfeld, H. Jiao and N. J. R. Van Eikema Hommes, *J. Am. Chem. Soc.*, 1996, **118**, 6317–6318.

[32] I. Fernández, J. I. Wu and P. Von Ragué Schleyer, *Org. Lett.*, 2013, **15**, 2990–2993.

[33] L. Nyulászi and P. Von Ragué Schleyer, *J. Am. Chem. Soc.*, 1999, **121**, 6872–6875.