A Journal of the Gesellschaft Deutscher Chemiker

Angewandte Chemie

GDCh

International Edition

www.angewandte.org

Accepted Article

Title: Tunable Mechanical Response from a Crystal Undergoing Topochemical Dimerization: Instant Explosion at Faster Rate and Chemical Storage of 'Harvestable Explosion' at Slower Rate

Authors: Kana M Sureshan and Arthi Ravi

To be cited as: *Angew. Chem. Int. Ed.* 10.1002/anie.201804589
Angew. Chem. 10.1002/ange.201804589

Link to VoR: http://dx.doi.org/10.1002/anie.201804589
http://dx.doi.org/10.1002/ange.201804589

WILEY-VCH

10.1002/anie.201804589

Tunable Mechanical Response from a Crystal Undergoing Topochemical Dimerization: Instant Explosion at Faster Rate and Chemical Storage of 'Harvestable Explosion' at Slower Rate

Arthi Ravi and Kana M. Sureshan*

Dedicated to Prof. K. N. Ganesh on his 65th birthday

Abstract: Strain developed in crystals in response to stimuli, causes mechanical response. Methods to tune such mechanical response is important for practical applications. Here we report that crystals of monomer **1**, having azide and alkyne units pre-organized in a ready-to-react orientation, undergo thermal topochemical dimerization to dimer **2** and show rate-dependent mechanical response. When the reaction rate is fast, the crystals explode violently. When the reaction rate is slow, the crystals absorb water from the surroundings contemporaneously with the reaction to form the dimer-hydrate in a single-crystal-to-single-crystal (SCSC) manner. Crystals of dimer-hydrate upon dehydration also undergo explosion. Thus, at slow reaction rate, the strain gets stored in crystals by hydration and the explosion can be harvested, at will, by dehydration. Use of this rate-dependent explosion in the automatic activation of a remedial electrical circuit in case of sudden rise in temperature has been demonstrated.

Materials that respond to various stimuli are of great interest in view of their possible applications in electronics, sensing, smart materials *etc*.[1] There is a growing interest in stimuli responsive crystals recently. Crystals respond to stimuli *viz.* light, heat, pressure *etc*.[2] primarily by molecular processes such as polymorphic transition,[3] chemical reaction,[4] isomerization,[5] or conformational change to form daughter-phase. The growth of daughter-phase in the parent-phase develops strain in the crystal,[2a,6] and to release this strain, such crystals show some macroscopic mechanical response[2a] in addition to the basic molecular processes. While elastic crystals release the strain as and when developed by slow and continuous mechanical reconfiguration such as bending,[4g-i,7] twisting,[4e-h] curling,[5b] rolling,[4i] change of size and shape[8] *etc*., plastic crystals, on the other hand, build up the strain to a critical level and then suddenly release by jumping, exploding, cracking *etc*.[3b-c,4a-c,9] In either case, the stimuli-induced strain-energy cannot be stored in the crystal for longer durations. A remarkable advancement in this area would be to store the strain energy in the single crystal itself for future harvest of the mechanical response at will. Here we report a topochemically-reactive crystal that, at faster reaction-rate, releases the developed strain instantly by explosion and, at slower rate, store the strain by absorbing water from the surroundings contemporaneously with the reaction in a single-crystal-to-single-crystal (SCSC) pathway and releases this stored strain later upon dehydration.

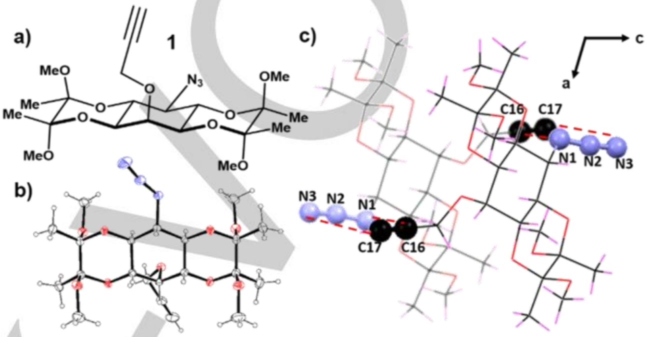


Figure 1. a) Chemical structure and b) ORTEP diagram of compound **1**. The thermal ellipsoids are at 30% probability. c) Head-to-tail centrosymmetric non-covalent dimer of compound **1** showing the juxtaposed azide and alkyne motifs. The reacting motifs are highlighted as ball and stick.

Monomers decorated with azide and alkyne groups can give triazole-linked polymers *via* Cu(I)-catalyzed click reaction.[10] There are also a few reports that they can undergo uncatalyzed polymerization *via* proximity-driven cycloaddition reaction in solid state.[11,4e] We have synthesized the monomer **1** (Supporting Information) having azide and alkyne groups (Figure 1a) and crystallized from 1:1 ethyl acetate/hexane mixture (Figure 1b, Table S1). Crystal structure of compound **1**, determined by Single-Crystal X-ray Diffraction (SCXRD) revealed that the molecules form a head-to-tail centrosymmetric supramolecular dimer through weak C-H…N hydrogen bond (Figure S1). Several other interactions stabilize such a packing (Table S2). The reaction partners in the dimer are juxtaposed parallelly as in the transition state for their cycloaddition reaction. The distances between the termini of azide and alkyne moieties (4.0 Å and 3.6 Å) are apt for their topochemical cycloaddition reaction (Figure 1c).[12] Crystals of compound **1** are stable at room temperature for several months. But at temperatures above 50 ºC, the crystals react to form the1,5-triazolyl linked cyclic dimer **2** (Supporting Information Section 3) as the only product, as a result of regiospecific 1,3-dipolar cycloaddition between azide and alkyne as expected from the crystal structure of compound **1**. The progress of the reaction was followed using time-dependent ^{1}H NMR, IR, DSC and PXRD techniques by withdrawing small portions of the heated sample at different time intervals and these experiments revealed that the dimerization reaction happens under topochemical control (Supporting Information Section 6, Figure S2).

It was observed that the crystals of monomer **1** do not melt even at very high temperature (300 ºC) but interestingly explode at around 190 ºC. To investigate this further, we have heated several crystals of **1** on a hot-stage microscope at a heating rate

---

[a] A. Ravi, Prof. Dr. K. M. Sureshan
School of Chemistry, Indian Institute of Science Education and Research Thiruvananthapuram, Vithura – 695551 (India)
E-mail: kms@iisertvm.ac.in
Supporting information can be found under https://doi.org/10.10xxx. CCDC 1829360-1829362 contain the supplementary crystallographic data for this paper. These data are provided free of charge by The Cambridge Crystallographic Data Centre.

of 5 ºC/min. All the crystals exploded, and the debris scattered all around (Movie S1). ^{1}H NMR spectroscopy and HRMS analysis of the debris formed after the explosion showed that it contains only dimer **2** (Figure S3). This implies that the explosion happens after the complete dimerization reaction.

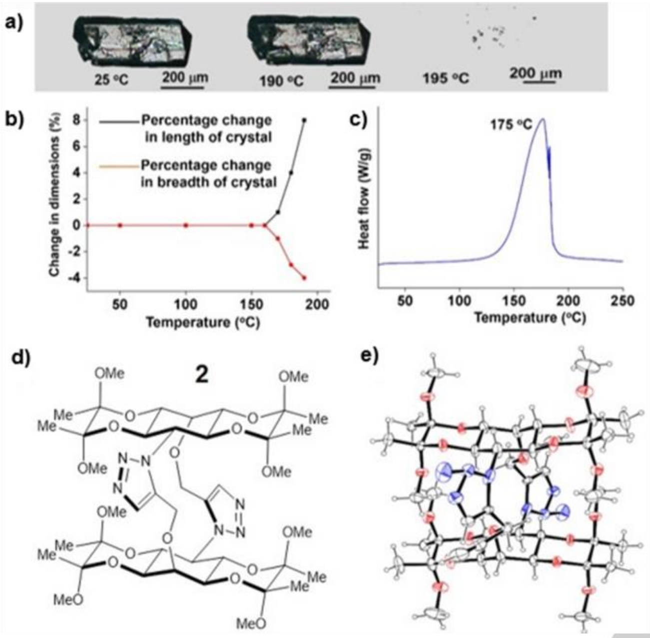


Figure 2. a) Optical microscopy images of a single crystal heated at 5 ºC/min at various stages. b) Plot of change in dimensions of crystal of monomer **1** with temperature. c) DSC thermogram of monomer **1** (rate of heating is 5 ºC/min). d) Chemical structure of dimer **2**. e) ORTEP diagram of partially reacted monomer showing the fragments of both monomer and dimer. The thermal ellipsoids are at 20% probability.

It was found that the crystals change their dimensions prior to bursting (Figure 2a). A plot of % change in dimensions against temperature revealed that, at all heating rates, the length of the crystal increased, and the breadth of the crystal decreased gradually and an abrupt change in dimension was observed just before the explosion (Figure 3b, Figure S4). The temperature (175 ºC) at which this sudden dimensional-change happens coincided with the temperature at which the maximum topochemical reaction occurs. DSC profile of crystals of **1**, at a heating rate of 5 ºC/min, suggested that the maximum reaction happens at 175 ºC (Figure 2c). This suggests that the change in crystal dimensions may be due to the topochemical reaction.

To understand the molecular level changes responsible for this macroscopic change, crystal structure of a single crystal was solved by SCXRD at its elongated stage just before explosion. For this, a single crystal of compound **1** was heated at a heating rate of 5 ºC/min under a hot stage optical microscope. When the temperature reached 190 ºC, maximum change in crystal dimensions was observed and at this point it was cooled and then analyzed by single crystal X-ray diffraction. The crystal contained both the dimer **2** (66%) and the monomer **1** (34%). The crystal structure of this partially reacted crystal suggests that the dimerization happens in a single-crystal-to-single-crystal manner even at high temperature (Figure 2e). Though the space group remained unchanged ($P2_1/c$), the unit cell dimensions changed due to the reaction. While the unit cell parameter ‘a’ expanded by 2.8%, ‘b’ and ‘c’ contracted by 2% and 2.5% respectively (Table S1) and resulted in an overall reduction of volume by 1.8%. Clearly, the macroscopic changes in the crystal dimensions arise from these changes in unit cell dimensions.

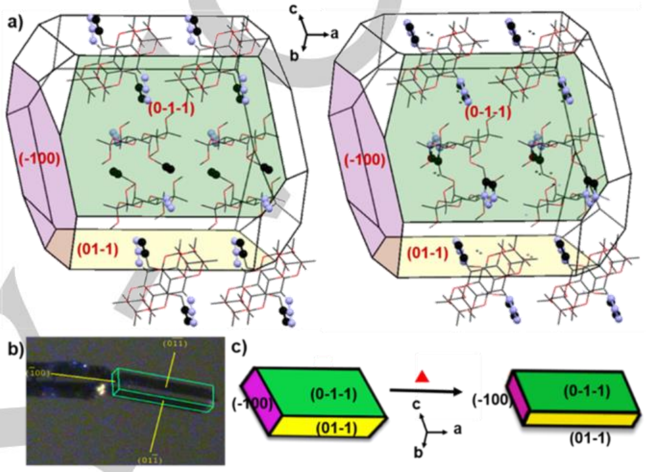


Figure 3. a) BFDH morphology of monomer **1** and partially reacted crystal. b) Face-indexing of single crystal of monomer **1** with the respective faces assigned. c) Schematic representation of single crystal of monomer **1** expanding along a-direction and contracting along the b- and c-directions.

The Bravais-Friedel-Donnay-Harker (BFDH) morphology of the crystal of monomer **1** and partially reacted crystal were determined from the diffraction data (Figure 3a). Face-indexing of a few single crystals of monomer **1** were carried out to identify various faces of the crystals (Figure 3b). To correlate the molecular-level changes with the macroscopic change, the faces determined from crystal structure morphology were matched with that of face-indexed crystals. This comparison revealed that the cycloaddition between juxtaposed azide-alkyne moieties occur along c- and b-axes (corresponding to breadth and thickness of the crystal), and the monomer molecules must move closer to achieve the reaction (Figure 3). This accounts for the shrinking of crystal along the breadth and height, during product formation. As no reaction occurs along the length of the crystal (a-direction) and the intermolecular interactions are weak along this direction (Figure S5), the crystal undergoes elongation to compensate for the contraction along breadth and thickness (to avoid large change in the volume).

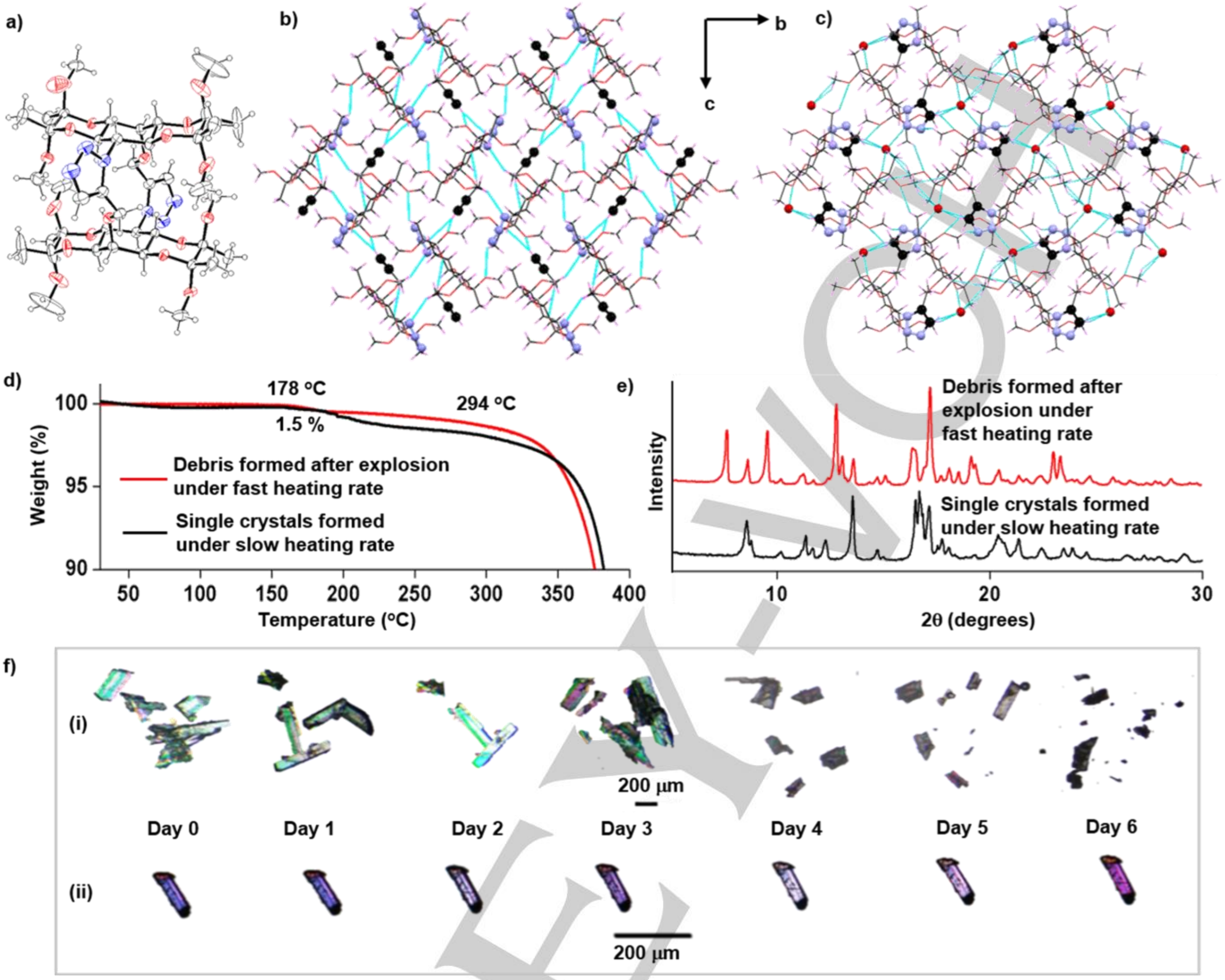


Figure 4. a) ORTEP diagram of dimer **2**.H_2O. The thermal ellipsoids are at 30% probability. b) Packing arrangement of monomer **1** stabilized by C-H…O and C-H…N hydrogen bonds. c) Packing arrangement of dimer **2**.H_2O in the 'bc' plane stabilized by weak (C-H…O and C-H…N) and strong (O-H…O & O-H…N) hydrogen bonding; Dimer molecules are bridged by water molecules and due to this the dimer **2**.H_2O is stabilized by more number of interactions compared to the monomer. d) TGA analyses of dimer formed under slow and fast heating rate. The dimer formed under slow heating rate shows a weight loss of 1.5% starting at 178 °C. e) Comparison of PXRD spectra of the dimer formed under slow and fast heating. f) Moisture dictates! Snapshots of the monomer crystals heated at 90 °C for 6 days in (i) dry (inert) condition; the crystals of monomer **1** convert to dimer **2** but crumble to powder. (ii) open (humid) condition; the crystals of monomer **1** convert to dimer **2**.H_2O in a SCSC manner.

In order to see whether we can control the mechanical response and get fully reacted single-crystal, the rate of the reaction was slowed down by keeping the crystals of **1** at a constant temperature of 90 °C. The reaction was complete in 132 h. To our delight, the single crystals were intact even after complete reaction. We have solved the crystal structure of one of these crystals by using SCXRD analysis. It is gratifying to note that the topochemical dimerization of monomer **1** proceeded quantitatively in a SCSC fashion with preservation of the space group (Table S1). In addition to the dimer **2**, one water molecule per dimer was also found in the crystal lattice (Figure 4a). Each water molecule is tetrahedrally coordinated to four molecules of dimer **2** through OH…N, OH…O and CH…O hydrogen bonds (Figure S5, Figure 4c). In 'bc' plane each dimer **2** molecule is non-covalently bridged through water molecules to six other dimer molecules arranged in a hexagonal arrangement (Figure 4c). Several weak CH…O and CH…N H-bonds also stabilize such connectivity (Table S2). Along "a" axis, dimer molecules are connected through weak van der Waal interactions (Figure S5).

From the crystal structure, it is clear that the water molecule stabilizes the crystal of the dimer **2**. TGA of **2**.H_2O revealed that the water molecules escape from the crystal only at very high temperature of 178-294 °C (Figure 4d). This is not surprising as each water molecule is connected to four dimer molecules through two hydrogen bonds and two CH…O H-bonds (Figure 4c, Table S2). A comparison of PXRD profiles of the debris formed *via* explosion of crystals under fast heating rate and the single crystals formed *via* SCSC transition under slow heating rate revealed that the packing of these two crystals are different (Figure 4e). TGA of the debris formed after explosion of the crystal, under fast heating rate (5 ^{o}C/min), proved the absence of water in them (Figure 4d).

In order to check the role of water in the SCSC nature of the reaction, crystals of **1** was heated in a dry atmosphere (glove box) at 90 ^{o}C, the same temperature at which the reaction followed an SCSC pathway in an open atmosphere, and regularly monitored by ^{1}H NMR as before. The reaction proceeded as expected and at the same rate as the reaction in an open atmosphere of relative humidity 50%. However, the crystal gradually lost its transparency and slowly crumbled into a heap of powder at the end of 132 h (Figure 4f). Thus, the reaction under open atmosphere follows a SCSC pathway (vide supra), but under dry conditions the reaction leads to the loss of crystal-integrity. This clearly establishes that water is essential for the reaction to proceed in a SCSC fashion.

A comparison of the crystal structures of monomer **1** and dimer **2** reveals that the monomer molecules in the non-covalent centrosymmetric dimer move closer by approximately 1Å during the reaction (Supporting Information Section 9, Figure S6) and this generates free space (cavity) in the crystal lattice (Figure S6). Crystals in general prefer close packing [13] and the empty volume generated as a result of the reaction causes strain in the crystals. In addition, the heat liberated due to the exothermic reaction contributes to the overall strain. The fate of the reacting crystal depends on the rate of the reaction (heating rate). When the rate of the reaction is fast, huge strain is generated rapidly and to relax this strain, the crystal undergoes sudden dimensional change (shrinking along its breadth and thickness and consequent elongation) to such an extent that the crystal cannot retain its structural integrity and hence undergoes explosion. When the rate of the reaction is sufficiently slow, the free space (and hence the strain) is created slowly and this would allow gradual absorption of water from the surroundings to fill these cavities contemporaneously with the reaction to form a stable stoichiometric hydrate in a SCSC fashion till the end of the reaction. In this case, as the rate of strain development is slow, the crystal is stabilized through slow hydration.

It is clear that without water, the crystal of **2** is unstable (strained) and hence explodes. We were curious to see whether the removal of water from crystals of **2**.H_2O will regenerate the strain in the crystal and thus show mechanical response. To investigate this, we have heated a few crystals of **2**.H_2O on a hot-stage microscope at heating rate of 5 ^{o}C/min (Movie S2). We found that when the temperature reached around 180 ^{o}C, the crystal exploded. It is to be recalled that TGA at this heating rate suggested that the dehydration occurs at this temperature (Figure 4d). Thus, it is clear that when water is removed, the crystals regain the strain and undergo explosion. This is the first case showing that the strain generated in a crystal due to a stimulus can be stored in the crystal itself and can be harvested as and when required. Controlling the mechanical response by modulating the external stimuli is of great significance.[14]

We envisioned the utility of such heating-rate dependent exploding-crystals for the activation of remedial electrical circuits in an unmanned mission or machinery in case of a sudden rise in temperature. To demonstrate such a practical application, we made an electrical circuit comprising of a DC power source, an LED strip as the load and a single crystal of **1** as the switch (Figure 5). In the experimental setup, one of the terminals is connected to a conducting plate, on which a single crystal was placed, and the other terminal was placed above the crystal. As the insulator crystal separates the electrodes, at ambient temperature the circuit is in 'OFF' state. However, upon heating the plate, the crystal exploded, and the circuit was switched 'ON' (Movie S3).

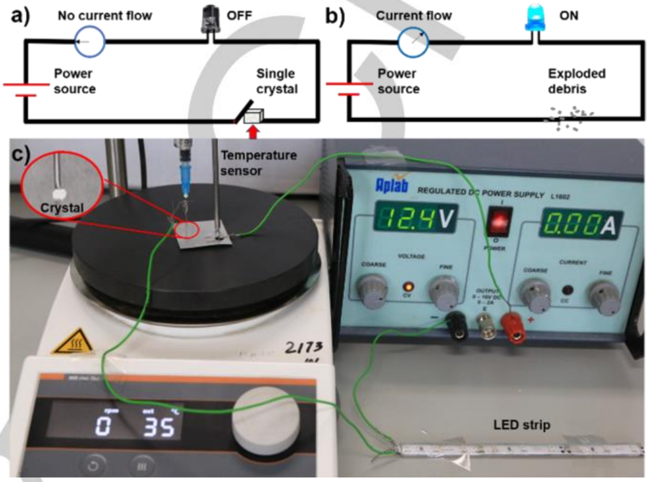


Figure 5. a) and b) Schematic representation of the electrical circuit in which crystals of compound **1** were used as a switch; c) Photograph of the electrical circuit.

In conclusion, we reported a thermal dimerization of a monomer, having azide and alkyne groups, to its cyclic dimer *via* dipolar cycloaddition reaction. The ready-to-dimerize pre-organized arrangement of monomer molecules facilitates regiospecific topochemical dimerization in the crystal. Though the dimerization reaction proceeds topochemically at all heating rates, the rate of the reaction dictates the fate of the reacting crystal. When the rate is fast, the crystal explodes violently due to the sudden increase in the strain and when the rate is slow the reaction follows a silent SCSC pathway by absorbing water molecules from surroundings forming a hydrate. By this hydrate formation, the strain developed slowly due to the slow topochemical reaction is stored in the crystal itself and up on dehydration, these hydrated crystals exhibit violent explosion. Apart from this interesting storage of stimuli-induced strain and its possible harvest at will, the heating rate-dependent explosion might find application in the design of turn on switches for activation of remedial electrical circuit without human intervention in case of sudden rise in temperature.

Acknowledgements

K.M.S. thanks Department of Science and Technology for a SwarnaJayanti Fellowship (DST/SJF/CS02/2012-13)

Keywords: cycloaddition • dimerization • exploding crystals • mechanical response • electrical switch

[1] a) C. J. Kloxin, C. N. Bowman, *Chem. Soc. Rev.* **2013**, *42*, 7161; b) R. Verduzco, *Science* **2015**, *347*, 949; c) S. Iamsaard, S. J. Aßhoff, B.

Matt, T. Kudernac, J. J. L. M. Cornelissen, S. P. Fletcher, N. Katsonis, *Nat. Chem.* **2014**, *6*, 229.

[2] a) P. Naumov, S. Chizhik, M. K. Panda, N. K. Nath, E. Boldyreva, *Chem. Rev.* **2015**, *115*, 12440; b) N. K. Nath, M. K. Panda, S. C. Sahoo, P. Naumov, *CrystEngComm* **2014**, *16*, 1850; c) O. Sato, *Nat. Chem.* **2016**, *8*, 644; d) G. R. Krishna, R. Devarapalli, G. Lal, C. M. Reddy, *J. Am. Chem. Soc.* **2017**, *138*, 13561; e) S. Saha, G. R. Desiraju, *J. Am. Chem. Soc.* **2017**, *139*, 1975.

[3] a) Z. S. Yao, M. Mito, T. Kamachi, Y. Shiota, K. Yoshizawa, N. Azuma, Y. Miyazaki, K. Takahashi, K. Zhang, T. Nakanishi, S. Kang, S. Kanegawa, O. Sato, *Nat. Chem.* **2014**, *6*, 1079; b) S. C. Sahoo, S. B. Sinha, M. S. R. N. Kiran, U. Ramamurty, A. F. Dericioglu, C. M. Reddy, P. Naumov, *J. Am. Chem. Soc.* **2013**, *135*, 13843; c) M. K. Panda, R. Centore, M. Causà, A. Tuzi, F. Borbone, P. Naumov, *Sci. Rep*. **2016**, *6*, 29610.

[4] a) A. Natarajan, C. K. Tsai, S. I. Khan, P. McCarren, K. N. Houk, M. A. Garcia-Garibay, *J. Am. Chem. Soc.* **2007**, *129*, 9846; b) R. Medishetty, A. Husain, Z. Bai, T. Runčevski, R. E. Dinnebier, P. Naumov, J. J. Vittal, *Angew. Chem. Int. Ed.* **2014**, *53*, 5907; *Angew. Chem.* **2014**, *126*, 6017; c) E. Hatano, M. Morimoto, T. Imai, K. Hyodo, A. Fujimoto, R. Nishimura, A. Sekine, N. Yasuda, S. Yokojima, S. Nakamura, K. Uchida, *Angew. Chem. Int. Ed.* **2017**, *56*, 12576; *Angew. Chem.* **2017**, *129*, 12750; d) S. Kobatake, S. Takami, H. Muto, T. Ishikawa, M. Irie, *Nature* **2007**, *446*, 778; e) R. Rai, B. P. Krishnan, K. M. Sureshan, *Proc. Natl. Acad. Sci. U.S.A.* **2018**, *115*, 2896; f) D. Kitagawa, H. Tsujioka, F. Tong, X. Dong, C. J. Bardeen, S. Kobatake, *J. Am. Chem. Soc.* **2018**, *140*, 4208; g) T. Kim, L. Zhu, L. J. Mueller, C. J. Bardeen, *J. Am. Chem. Soc.* **2014**, *136,* 6617; h) L. Zhu, R. O. Al-Kaysi, C. J. Bardeen, *Angew. Chem. Int. Ed.* **2016**, *55*, 7073; *Angew. Chem.* **2016**, *128*, 7189; i) H. Wang, P. Chen, Z. Wu, J. Zhao, J. Sun, R. Lu, R. *Angew. Chem. Int. Ed.* **2017**, *56*, 9463; *Angew. Chem.* **2017**, *129*, 9591.

[5] a) O. S. Bushuyev, A. Tomberg, T. Friščić, C. J. Barrett, *J. Am. Chem. Soc.* **2013**, *135*, 12556; b) T. Kim, M. K. Al-Muhanna, S. D. Al-Suwaidan, R. O. Al-Kaysi, C. J. Bardeen, *Angew. Chem. Int. Ed.* **2013**, *52*, 6889; *Angew. Chem.* **2013**, *125*, 7027.

[6] P. Commins, I. T. Desta, D. P. Karothu, M. K. Panda, P. Naumov, *Chem. Commun*. **2016**, *52*, 13941.

[7] a) S. H. Mir, Y. Takasaki, E. R. Engel, S. Takamizawa, *Angew. Chem. Int. Ed.* **2017**, *56*, 15882; *Angew. Chem.* **2017**, *129*,16098; b) A. Worthy, A. Grosjean, M. C. Pfrunder, Y. Xu, C. Yan, G. Edwards, J. K. Clegg, J. C. McMurtrie, *Nat. Chem.* **2018**, *10*, 65.

[8] a) M. Irie, S. Kobatake, M. Horichi, *Science* **2001**, *291*, 1769; b) K.-J. Chen, Y.-C. Tsai, Y. Suzaki, K. Osakada, A. Miura, M. Horie, *Nat. Commun.* **2016**, *7*, 13321.

[9] a) R. Medishetty, S. C. Sahoo, C. Mulijanto, P. Naumov, J. J. Vittal, *Chem. Mater.* **2015**, *27*, 1821; b) M. K. Panda, T. Runcevski, A. Husain, R. E. Dinnebier, P. Naumov, *J. Am. Chem. Soc*. **2015**, *137*, 1895; c) S. Ghosh, M. K. Mishra, S. Ganguly, G. R. Desiraju, *J. Am. Chem. Soc.* **2015**, *137*, 9912; d) D. Kitagawa, T. Okuyama, R. Tanaka, S. Kobatake *Chem. Mater.* **2016**, *28*, 4889.

[10] a) Y. Chen, Z. Guan, *J. Am. Chem. Soc.* **2010**, *132*, 4577; b) S. Hartwig, S. Hecht S. *Macromolecules* **2010**, *43*, 242.

[11] a) W. Li, X. Li, W. Zhu, C. Li, D. Xu, Y. Ju, G. Li, *Chem. Commun*. **2011**, *47*, 7728; b) B. P. Krishnan, R. Rai, A. Asokan, K. M. Sureshan, *J. Am. Chem. Soc.* **2016**, *138*, 14824; c) Pathigoolla, A.; Sureshan, K. M. *Angew. Chem. Int. Ed.* **2014**, *53*, 9522; *Angew. Chem.* **2014**, *126*, 9676.

[12] G. M. J. Schmidt, *Pure*. *Appl*. *Chem*. **1971**, *27*, 647.

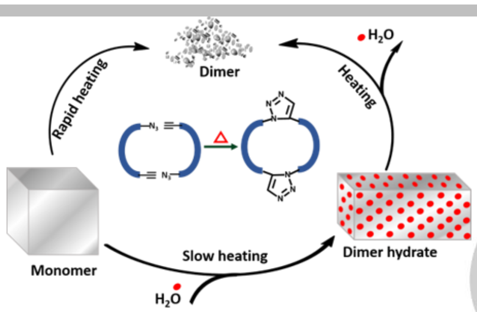
[13] I. Hargittai, *Struct. Chem.* **2014**, *25*, 1321.

[14] A. A. Matvienko, D. V. Maslennikov, B. A. Zakharov, A. A. Sidelnikov, S. A. Chizhik, E. V. Boldyreva, *IUCrJ* **2017**, *4*, 588.

Entry for the Table of Contents

COMMUNICATION

Crystals of an azide-and-alkyne functionalized cyclitol derivative undergo topochemical azide-alkyne cycloaddition reaction to form its cyclic dimer. When the reaction-rate is faster, the crystals explode and when it is slower, the crystal absorb water from the surroundings to form the hydrated-dimer in a single-crystal-to-single-crystal manner, which upon dehydration explodes violently. Thus, hydration stores the strain and dehydration releases it.



*Arthi Ravi, Kana M. Sureshan**

Page No. – Page No.

Tunable Mechanical Response from a Crystal Undergoing Topochemical Dimerization: Instant Explosion at Faster Rate and Chemical Storage of 'Harvestable Explosion' at Slower Rate