





Subscriber access provided by UNSW Library

Cracking Under Internal Pressure: Photodynamic Behavior of Vinyl Azide Crystals Through N2 Release

Dylan J Shields, Durga Prasad Karothu, Karthik Sambath, Ranaweera A. A. Upul Ranaweera, Stefan Schramm, Alexander Duncan, Benjamin Duncan, Jeanette A. Krause, Anna D. Gudmundsdottir, and Pance Naumov

J. Am. Chem. Soc., Just Accepted Manuscript • DOI: 10.1021/jacs.0c07830 • Publication Date (Web): 29 Sep 2020

Downloaded from pubs.acs.org on October 1, 2020

Just Accepted

"Just Accepted" manuscripts have been peer-reviewed and accepted for publication. They are posted online prior to technical editing, formatting for publication and author proofing. The American Chemical Society provides "Just Accepted" as a service to the research community to expedite the dissemination of scientific material as soon as possible after acceptance. "Just Accepted" manuscripts appear in full in PDF format accompanied by an HTML abstract. "Just Accepted" manuscripts have been fully peer reviewed, but should not be considered the official version of record. They are citable by the Digital Object Identifier (DOI®). "Just Accepted" is an optional service offered to authors. Therefore, the "Just Accepted" Web site may not include all articles that will be published in the journal. After a manuscript is technically edited and formatted, it will be removed from the "Just Accepted" Web site and published as an ASAP article. Note that technical editing may introduce minor changes to the manuscript text and/or graphics which could affect content, and all legal disclaimers and ethical guidelines that apply to the journal pertain. ACS cannot be held responsible for errors or consequences arising from the use of information contained in these "Just Accepted" manuscripts.

is published by the American Chemical Society. 1155 Sixteenth Street N.W., Washington, DC 20036

Published by American Chemical Society. Copyright © American Chemical Society. However, no copyright claim is made to original U.S. Government works, or works produced by employees of any Commonwealth realm Crown government in the course of their duties.

7

Cracking Under Internal Pressure: Photodynamic Behavior of Vinyl Azide Crystals Through N₂ Release

Dylan J. Shields, Durga Prasad Karothu, Karthik Sambath,[‡] Ranaweera A. A. Upul Ranaweera,[‡] Stefan Schramm, Alexander Duncan, Benjamin Duncan, Jeanette A. Krause, Anna D. Gudmundsdottir,* and Panče Naumov*

ABSTRACT: When exposed to UV light, single crystals of the vinyl azides 3-azido-1-phenylpropenone (1a), 3-azido-1-(4-methoxyphenyl)propenone (1b), and 3-azido-1-(4-chlorophenyl)propenone (1c) exhibit dramatic mechanical effects by cracking or bending with the release of N_2 . Mechanistic studies using laser flash photolysis, supported by quantum mechanical calculations, show that each of the vinyl azides degrades through a vinylnitrene intermediate. However, despite having very similar crystal packing motifs, the three compounds exhibit distinct photomechanical responses in bulk crystals. While the crystals of 1a delaminate and release gaseous N_2 indiscriminately under paraffin oil, the crystals of 1b and 1c visibly expand, bend, and fracture, mainly along specific crystallographic faces, before releasing N_2 . The photochemical analysis suggests that the observed expansion is due to internal pressure exerted by the gaseous product in the crystal lattices of these materials. Lattice energy calculations, supported by nanoindentation experiments, show significant differences in the respective lattice energies. The calculations identify critical features in the crystal structures of 1b and 1c where elastic energy accumulates during gas release, which correspond to the direction of the observed cracks. This study highlights the hitherto untapped potential of photochemical gas release to elicit a photomechanical response and motility of photoreactive molecular crystals.

1. Introduction

The quest for new smart organic materials capable of transducing light and other stimuli into mechanical motion has intensified in recent years because of their potential in a number of applications, including electronics, biomedicine, and soft robotics. Specifically, these materials show promise for applications in smart sensors, electronics, and medical devices.1-⁴ Historically, polymers and elastomers were among the first organic materials to be studied and applied as smart materials; however, owing to limitations associated with their disordered structures, there is now a demand for alternative materials endowed with long-range structural order that can transduce energy and respond faster while still being light in weight. Adaptive molecular crystals have recently been shown to be able to perform many of the same mechanical feats as their polymeric predecessors.⁵⁻⁹ These previously underexplored materials can respond rapidly to external stimuli such as light, heat, or mechanical force by switching between different crystal packing arrangements (polymorphs) or by undergoing chemical reactions such as cyclization, cis-trans isomerization, or dimerization.¹⁰ The underlying molecular reconfiguration generates a considerable strain in the crystal lattice, which is manifested as macroscopically visible motion such as bending, shattering, jumping, or flipping.11

An alternative, unexplored approach for eliciting motility in crystalline materials is to acquire momentum by releasing a gas, a mechanism that is analogous to the operation of a gasoline engine. A prominent recent example of crystal motion by gas release is the thermally induced coupling of a zwitterionic metal complex reported by Ovcharenko *et al.*^{12–14}Although this phenomenon was attributed to the release



Chart 1. Molecular structures of 3-azido-1-phenylpropenone (1a), 3-azido-1-(4-methoxyphenyl)propenone (1b), and 3-azido-1-(4-chlorophenyl)propenone (1c).

of oxygen gas as a product of the reaction, the direct correlation of the reaction mechanism with the kinematic traits of the phenomenon was not conducted. Except for some early reports in some inorganic compounds,^{15–19} other reports on mechanical movements caused by gas release are scarce, consisting of brief mentions or anecdotal reports in presentations. Thus, this study aimed to provide an in-depth understanding of the photodynamic behavior of the crystals of three structurally related gas-releasing azido compounds (Chart 1) using a combined experimental and computational approach to study the underlying reaction mechanism. The crystals of 3-azido-1-phenylpropenone (1a), 3azido-1-(4-methoxyphenyl)propenone (1b) and 3-azido-1-(4chlorophenyl)propenone (1c), whose molecular structures differ only by the *para*-substituent with respect to the ketone group, were found to have similar packing motifs but very different photomechanical responses. The driving forces responsible for crystal disintegration and motility were elucidated using video microscopy and by correlating the observed deformation, gas release, and motion to the structural and molecular modeling results. In addition to the kinematic study, the mechanism of denitrogenation was also investigated in solution and in the solid state through product studies and laser flash photolysis.

58

59

2.1. Product Analysis

1

2

3

4

5

6

7

8

9

10

11

12

13

14

15

16

17

18

19

20

21

22

23

24

25

26

27

28

29

30

31 32

33

34

35

36

37

38

39

40

41

42

43

44

45

46

47

48

49

50

51

52

53

54

55

56

57 58 59

60

The irradiation of the vinyl azides **1a-c** with UV light (Hg arc lamp, Pyrex) in argon-saturated chloroform-d resulted in the corresponding azirines 3, isoxazoles 4, and cyanides 5, as depicted in Scheme 1. The reaction progress, followed by ¹H-NMR spectroscopy, showed that the photoproduct ratio changed as a function of irradiation time, with continuous irradiation of the reaction mixture increasing the yield of cyanides 5 at the expense of azirines 3 and isoxazoles 4. These results are in accord with the established photolysis behavior of 1a.20 In contrast, the irradiation of the crystals of vinyl azides 1a-c pressed between glass slides selectively yielded azirines 3a-c. As azirines **3a–c** are highly reactive, isolation using traditional column chromatography was not feasible. Instead, products 3, 4, and 5 were identified in the reaction mixture based on IR and NMR spectroscopic evidence. The recorded spectra of 4a-c and 5a-c were consistent with those available in the literature.²¹⁻²⁵ To support the characterization of azirines **3a-c**, we compared their ¹H-NMR spectra to those reported for 2-benzoyl-2-methyl-2H-azirine and 2-methyl-2-phenyl-2H-azirine, in which the vinylic hydrogen atom on the azirine ring is observed at 9.75 and 9.80 ppm, respectively,²² corresponding to that in azirine 3 at 9.67 ppm. Similarly, the α -hydrogen atom in azirine **3** is located at 3.5 ppm, which is similar to the chemical shift observed for the α -hydrogen atom of 2-benzoyl-3-methyl-2*H*-azirine at 3.50 ppm.²⁶



Scheme 1. Photoproducts obtained by irradiation of vinyl azides **1** in chloroform-*d* and as crystals.

To further aid with characterization, thermolysis was performed in chloroform-d solutions of vinyl azides 1a-c at 70 °C. The progress of the reaction was followed by ¹H-NMR spectroscopy, which demonstrated that vinyl azides 1a-c were cleanly transformed into azirines 3a-c and cyanides 5a-c. The ¹H-NMR signals for the vinyl protons of vinyl azides **1a-c** at 6.5 and 7.5 ppm were depleted and new signals for the protons on the azirine moiety appeared at 3.5 and 9.0 ppm. Thus, cyanides 5 are most likely formed both thermally and photochemically from azirines 3. The product studies clearly demonstrated that the photoreactions in the crystals are more selective than their counterparts in solution. The formation of azirines in the solid state is presumably more favorable than the formation of isoxazoles as less molecular movement is required, which is preferable in a spatially constrained, rigid environment. This reasoning is consistent with the topochemical postulate, which states that solid-state reactions should proceed via the pathway of least molecular motion.27 Based on the product formation, we theorize that upon exposure to light, vinyl azides 1a-c form their corresponding singlet excited states (S_1) that intersystem-cross efficiently to triplet 1,2-biradicals ³2BR, which then extrude a N_2 molecule to afford triplet vinvlnitrene intermediates ³2N (Scheme 2). Generally, triplet vinylnitrenes are short-lived intermediates that have significant 1,3-biradical character and intersystem-cross efficiently to form products.28,29



Scheme 2. Proposed mechanism for the formation of photoproducts 3, 4, and 5 from vinyl azides 1.

2.2. Laser Flash Photolysis

To verify that vinyl azides **1a–c** form products through vinylnitrene intermediates both in solution and in the solid state, we employed nanosecond laser flash photolysis studies. Laser flash photolysis of **1a–c** in argon-saturated acetonitrile gave transient spectra with absorption maxima between 340 and 360 nm (Figure 1A, Supporting Information Figures S1 and S2). The transient absorption was attributed to triplet vinylnitrene ³2N based on a comparison with the TD-DFT-calculated absorption spectrum (Figure 1B) and the observation that the absorption is quenched in oxygen-saturated acetonitrile.



Figure 1. (A) Transient spectra obtained by laser flash photolysis of **1b** in argon-saturated acetonitrile. (B) TD-DFT-calculated spectrum of vinylnitrene ³**2Nb** using C-PCM solvation and acetonitrile.

The decay of all transient absorptions in argon-saturated solutions were best fitted with a pseudo-first-order function, resulting in lifetimes of 10, 12, and 8 µs for vinylnitrenes ³2Na, ³2Nb, and ³2Nc, respectively. The transient absorptions formed

2

3

4

5

6

7

8

9

10

11

12

13

14

15

16

17

18

19

20

21

22

23

24

25

26

27

28

29

30

31

32

33

34

35

36

37

38

39

40

41

42

43

44

45

46

47

48

49 50

51

52 53 54

55

56

57

58 59

60

with rate constants of $\sim 2 \times 10^7$ s⁻¹, which correspond to the decay of the precursor 1,3-biradicals (³**2BR**). The laser flash photolysis studies demonstrate that solution photolysis of vinyl azides **1a–c** results in the formation of triplet vinylnitrenes and that the *p*-substituent does not significantly affect the reactivity while only slightly affecting the absorption profile.



Figure 2. Transient spectra obtained by laser flash photolysis of (A) **1a**, (B) **1b**, and (C) **1c** in argon-saturated nanocrystalline suspensions.

The laser flash photolysis of vinyl azides **1** was performed in nanocrystalline suspensions in accordance with literature procedures.³⁰ The transient absorption spectra obtained by laser flash photolysis of crystalline **1a–c** (Figure 2) are similar to

those obtained in solution with absorbance maxima between 350 and 380 nm, which are attributed to triplet vinvlnitrenes ³2Na**c**. However, the nanocrystalline suspension spectra are not fully quenched when the suspension is saturated with oxygen or air, presumably because the quenching mechanism in crystals is less efficient than in solution. Furthermore, an analysis of the kinetics in argon-saturated suspensions revealed that vinylnitrenes ³2Na, ³2Nb, and ³2Nc are longer lived than in solution, with lifetimes of 14, 12, and 14 µs, respectively. In comparison, in air- and oxygen-saturated nanocrystalline suspensions, the lifetimes of the triplet vinylnitrenes are reduced but not completely quenched. Importantly, the rate of formation of the vinylnitrenes from nanocrystalline suspensions of vinyl azides 1 became faster than the time resolution of the laser. Altogether, the laser flash photolysis studies of vinyl azides **1a-c** in nanocrystals demonstrate that in crystals, triplet vinylnitrenes are formed faster, are longer lived, and are less easily quenched by oxygen. However, vinylnitrenes ³2Na-c have remarkably similar lifetimes in the solid state.

2.3. Quantum Chemical Calculations

To further explore the photoreactivity of vinyl azides 1, TD-DFT calculations of their reactions were carried out using the B3LYP method in conjunction with the 6-31+G(d) basis set.^{31,32} The optimized minimal energy conformer of vinyl azide 1a showed that the molecule is fully conjugated and flat (Figure 3). The S_1 state of **1a** was calculated by TD-DFT to be 76 kcal mol⁻¹ higher in energy than its ground state (S_0) (Figure 4, left). The optimization of the triplet configuration of vinyl azide 1a revealed that it is best described as a 1,2-biradical, ³2BRa (Figure 3). The minimal energy conformer of 2BRa is 55 kcal mol^{-1} above its S₀ state (Figure 4A), and spin density calculations located the unpaired electrons on the C_{α} and C_{β} atoms, which were rotated ~90° away from each other to minimize the overlap between the radical centers (Figure 4B). The optimization of the structure of vinylnitrene ³2Na showed that this species exists as two conformers (trans and cis, Figure 3) corresponding to two energy minima, with the *trans* isomer being 5 kcal mol⁻¹ more stable than the *cis* isomer (Figure 4A). Furthermore, spin density calculations showed that vinylnitrene ³2Na has a significant 1,3-biradical character, and the rotational barrier around the vinylic bond is low (~14 kcal mol⁻¹) (Figure 4B). The calculated transition state barrier for the transformation of ³2BRa to vinylnitrene ³2Na was found to be very small (0.4 kcal mol⁻¹). Therefore, the calculations support the hypothesis that vinylnitrene ³2Na is easily formed from the excited state of vinyl azide 1a. Structural flexibility can explain the formation of both azirine **3a** and isoxazole **4a** in solution. The stationary points on the triplet surfaces of vinyl azides 1b and 1c, calculated using DFT, resulted in similar diagram as for vinyl azide 1a (Supporting Information Figures S3-S4). Furthermore, the calculated rotational barriers for vinylnitrenes ³2Nb and ³2Nc were comparable to that for vinylnitrene ³2Na (Supporting Information Figures S5-S6).



Figure 3. Optimized structures of 1a, ³2BRa, and two isomers of ³2Na. The numbers in the parenthesis are the calculated spin densities.



Figure 4. A) Calculated stationary points on the triplet surface of 1a. The energies are in kcal mol⁻¹. B) calculated rotational barrier for ³2Na.

2.4. Photomechanical and Disintegrative Effects

When the crystals of vinyl azide 1a were exposed to a 400nm LED and monitored using an optical microscope equipped with a camera, they were observed to fragment, shatter, and splinter violently as a result of the photochemical reaction (Figure 5A, Supporting Information Video 1). As the reaction progressed, the color of the translucent crystals and the debris changed from colorless to opaque amber. Due to violent fracturing of the crystals, the resulting debris had irregular and defective surfaces, and was not amenable to nanoindentation to determine their mechanical properties. To observe the evolution of gas, the crystals of azide 1a were covered in mineral oil and irradiated. The released N₂ appeared as bubbles emanating from the crystal

(Supporting Information Video 2). The bubbles formed and evolved from the crystals without a clear preference with respect to their edges or visible defect sites.



Figure 5. Optical microcopy images showing the photomechanical effects, cracking, and disintegration during the photochemical reactions of the crystals of **1a–c**. (A) Splintering of a crystal of **1a** upon irradiation. The approximate size of the crystal is $\sim 1.6 \times 0.5 \times 0.1$ mm. (B) Bending of the crystal of **1b** and development of parallel striations on the crystal surface due to cracking. The approximate size of the crystal is $\sim 1.5 \times 0.3 \times 0.1$ mm. (C) Bending and cracking of a crystal of **1c**. The approximate size of the crystal is $\sim 2 \times 0.5 \times 0.2$ mm. For recording of the effects, see Supporting Information Videos 1–7.

In stark contrast, the crystals of 1b were observed to visibly bend, expand, and then crack (Figure 5B, Supporting Information Video 3). Moreover, if they were not restrained, some of these crystals jumped off the surface (Supporting Information Video 4); however, no splintering or violent fragmentation was observed. At this point, it is not clear whether the expulsion of gas or the disintegration of the lattice are responsible for the acquired motility of the crystals and the ensuing debris. Since the crystal explosion occurs almost concomitantly with the gas release, these effects cannot be resolved by simple kinematic analysis. Another distinct difference was that the cracks in the crystals of 1b always developed perpendicular to the (010) face. When the irradiation of 1b was performed in mineral oil, the crystals retained the gaseous N2 before eventually releasing it at one of the cracks on the (010) face. Occasionally, the formation of a gas bubble could be observed in the crystal prior to cracking (Figure 6, Supporting Information Video 5). The crystals of 1c behaved similarly to those of 1b, in that exposure to light resulted in bending, expansion, and cracking (Figure 5C, Supporting Information Video 6) as well as some jumping (Supporting Information Video 7). The cracks in the crystals of 1c also formed perpendicular to the long axis, allowing for the release of N2 gas. The behavior of the crystals of 1c in oil resembles that of the crystals of 1b, with no N₂ released from the crystal until cracks

2

3

4

5

6

7

8

9

10

11

12

13

14

15

16

17

18

19

20

21

22

23

24

25

26

27

28

29

30

31

32

33

34

35

36

37

38

39

40

41

42

43

44

59

60

develop in the interior that appear as striations on the surface (Supporting Information Video 8).



Figure 6. Formation of a bubble inside a crystal of azide **1b** and its subsequent release. Owing to the transparent nature of the crystal, red lines have been added to highlight a pair of parallel crystal edges. See Supporting Information Video 5.

2.5. Crystal Structures and Mechanical Properties

The crystal structures of vinyl azides **1a-c** were determined and inspected for clues that may help elucidate the origin of the photomechanical effects. The crystals of vinyl azides 1a and 1b were both found to belong to the monoclinic $P2_1/n$ space group, whereas the crystals of 1c were in the triclinic $P\overline{1}$ space group. The intramolecular atomic distances are very similar in all three compounds, generally falling within the range of ± 0.1 Å for C=C, C-C(O), and C-N₃ bonds (Crystallographic Supporting Information). The main structural difference in molecular geometries was the torsion angle between the ortho carbon of the phenyl ring and the carbonyl oxygen; 1a and 1b have planar torsion angles of $\leq 1^{\circ}$, whereas that in 1c is 11° (Supporting Information Figure S7-S10). In the crystals, the molecules of 1a-c pack in sheet-like motifs (Figure 7). The centroid-tocentroid distances between the phenyl rings are all in the range 3.80–3.87 Å, suggesting weak π - π interactions. The shortest distance between the vinyl moieties (C_{α} -to- C_{α} , C_{β} -to- C_{β} , N_1 -to- N_1 , N_2 -to- N_2 and N_3 -to- N_3) of adjacent molecules are also similar for 1a and 1b. As the crystal packing of the three compounds is very similar, it cannot account for the differences in their photodynamic behavior.

45 The faces of typical crystal habits were indexed and related to 46 the respective crystal structures to identify any preferred 47 directions in the crystals for reactivity, bending, and gas release. As expected from the crystal symmetries, the crystal faces of 1c 48 are different from those of 1a and 1b (Figure 7). A comparison 49 of the packing diagrams and crystal faces indicated that 1b and 50 1c first show cracking on the (010) and (001) faces, respectively, 51 whereas 1a does not show a preferential face for chipping or 52 cracking. The directionality of cracking in 1b and 1c can be 53 rationalized by considering the intermolecular interactions. If 54 the interactions are sufficiently strong to overcome the elastic 55 energy, the gas remains inside the crystal during the course of 56 the photochemical reaction. It accumulates until a threshold in 57 the accumulated elastic energy is reached and a crack is 58

generated. The gas is expected to accumulate preferentially at locations in the crystal where the interactions are weakest or in any voids or channels in the structure. As more gas is generated. it eventually reaches the surface of the crystal, which is the (010)and (001) face for 1b and 1c, respectively. With this qualitative scenario in mind, the structure diagrams in Figure 7 indicate that all three crystal structures contain channels owing to their sheetlike packing motifs. The channels provide preferred sites for accumulation of gas. Being effective concentrators of the accumulated elastic energy, the first cracks are expected to appear at surface imperfections or other crystal defects that alleviate the stability of the lattice. This reasoning implies that the origin of the photomechanical motions lies within the difference in lattice energetics between the three crystals; 1a probably lacks sufficient energy to prevent cracking, whereas 1b and 1c likely possess more energy owing to their resistance to cracking. In an attempt to determine the structure of the products while they was generated inside the crystal interior, we resorted to X-ray photodiffraction (photocrystallography) by using different conditions. However, these efforts remained fruitless due to the proclivity of the crystal to crack and partially or completely disintegrate before significant amounts of the product could be generated for data collection and structure determination.

Because the deformation is related to mechanical compliance of the crystal, nanoindentation experiments were performed to determine if the crystal stiffness and hardness could explain the differences in the mechanical motions with gas release. Vinyl azides **1b** and **1c** were found to have elastic (Young's) moduli of 9.8 ± 0.5 GPa and 8.1 ± 0.7 GPa, respectively (Figure S11), attempts to obtain the elastic modulus of **1a** were unsuccessful owing to the brittle nature of its crystals. This result indicates that **1b** and **1c** are likely to have higher stiffnesses, which was subsequently confirmed using lattice energy calculations.



Figure 7. Molecular packing in the crystals of compounds **1a–c** before and during reaction, and correlation with the mechanical effects. (A,C,E) Superimposition of an optical images of single crystals of **1a** (A), **1b** (C) and **1c** (E) and the respective crystal structures before irradiation. (B,D,F) Optical images of the crystals of **1a** (B), **1b** (D) and **1c** (F) after irradiation, and model of the respective crystal structures at the initial stage of nitrogen release, before significant structure perturbation occurs. The channels are shown between the molecular columns where the nitrogen molecules are likely to accumulate before pressure builds up and induces peeling, bending and cracking of the crystals.

2.6. Lattice Energy Calculations

1

2

3

4

5

6

7

8

9

10

11

12

13

14

15

16

17

18

19

20

21

22

23

24

25

26

27

28

29

30

31

32

33

34

35

36

37

38

39

40

41

42

43

44

45

46

47

48

49

50

51

52

53

54

55

56

57

58 59

60

As lattice energies and anisotropy of intermolecular interactions appear to be the key to explaining the different photomechanical effects, the so-called energy frameworks³³ were calculated to provide a more quantitative description and to visualize the anisotropy of the intermolecular interactions in the crystals. The results, in Figure 8, showed that 1a features significantly weaker crystal interactions than 1b and 1c. In 1a, the strong interactions ranged between 15.2 and 33.9 kJ mol⁻¹ with weaker interactions of 6 kJ mol⁻¹. In comparison, **1b** had strong interactions ranging from 13.2 to 40.6 kJ mol⁻¹ and weak interactions of 11.7-12.9 kJ mol⁻¹. Similar to **1b**, **1c** had strong interactions of 18.4–41.5 kJ mol⁻¹ and weak interactions of 7.8–10.1 kJ mol⁻¹. These differences in the energy framework are responsible for the differences in the strength toward cracking between the weak, flaky crystals of 1a and the strong, mechanical crystals of 1b and 1c. The observation that 1b and 1c crack along a specific crystal face during irradiation implies that as N₂ gas is released within the crystals at locations where the intermolecular interactions are weakest. Support for this hypothesis is drawn from the correlation among the lattice energy calculations, crystal face indexing, and nanoindentation measurements.



Figure 8. Energy frameworks of vinyl azides **1a–c** (tube size = 80, energy cutoff = 5 kJ mol⁻¹). (A) **1a** has weak interactions of 6 kJ mol⁻¹ and strong interactions of 15.2–33.9 kJ mol⁻¹. (B) **1b** has weak interactions of 11.7–12.9 kJ mol⁻¹ and strong interactions of 13.2–40.6 kJ mol⁻¹. (C) **1c** has weak interactions of 7.8–10.1 kJ mol⁻¹ and strong interactions of 18.4–41.5 kJ mol⁻¹

Vinyl azide **1a** does not exhibit a preferential cracking direction. Instead, crystal surface delamination or random shattering occurs upon irradiation. Correspondingly, the lattice energy calculations showed that this compound has the weakest interactions. These very weak interactions cannot keep the crystal together effectively, resulting in random delamination and shattering. This observation is supported by the nanoindentation experiments, which confirmed that the crystals of **1a** were too brittle to provide a proper basis for crystal indentation. Lastly, the void spaces in this crystal are located near the area with the weakest lattice energy interactions. The void space location is significant because as the pressure of N_2 increases in these void spaces, the likelihood of overcoming the weak forces in this area increases, allowing cracks to appear.

In contrast, when the crystals of **1b** are irradiated, they consistently break along their (010) face. When this observation is compared to the lattice interaction calculations, as shown in Figure 8, the repeated cracks can reasonably be attributed to the breakdown of the weak interactions between the methoxy groups, which are the weakest interactions identified by the lattice energy calculations. Because these weak interactions are stronger than those in **1a**, the crystals of **1b** maintain their form and shape more effectively upon the release of nitrogen gas. This behavior is supported by the nanoindentation experiments, which showed that the crystals of azide **1b** had the highest Young's modulus. Again, the location of the void space corresponds well with the location of the weak interactions in the crystal, suggesting that the growing N_2 volume will eventually overcome the weak interactions.

Similar results were obtained when this rationale was applied to 1c. However, unlike those of 1b, upon irradiation the crystals of 1c crack perpendicular to the (001) face. When the lattice energy calculation is rotated perpendicular to the c axis to imitate this cracking action, the spaces in the cracks again align with the weak interactions between the chlorine substituents between the layers. Furthermore, the chlorine interactions are weaker than the methoxy interactions, which is supported by the nanoindentation data, which showed that 1c had a lower Young's modulus than 1b but presumably a higher Young's modulus than 1a. These weaker interactions are evident in the videos showing the decomposition of 1c (Supporting Information Video 7), in which the crystal shape is mostly maintained, similar to the crystals of 1b, but some crystals fragment and shatter, like the crystals of 1a. This behavior is in line with the weak lattice points identified by the lattice energy calculations being intermediate between those in 1a and 1b.

3. CONCLUSIONS

The reaction mechanism and photomechanical effects of vinyl azides 1a-c were thoroughly investigated. To the best of our knowledge, this is the first in-depth study of crystal disintegration and movements induced by gas release where the photomechanical effects are directly correlated with the structure in a set of structurally similar compounds. While the mechanistic details of the photochemical reactions in these crystals are well established from the transient spectra and the crystal structures of the unreacted crystals provides a solid basis to hypothesize the origin of the mechanical effects, the relation with the mechanical effect should be considered with some the three key processes-the precaution. Namely, photochemical reaction that results in formation and accumulation of gas, the formation of cracks, and finally the crystal explosion-occur on very different time scales that cover several orders of magnitude. The kinetics of the mechanical response is unlikely to follow the kinetics of the photochemical reaction because the formation of cracks requires accumulation of gaseous product and buildup of pressure up to a threshold value. Since the quantum yield of the reaction is low, this process requires significant amount of time and occurs on a Page 7 of 12

1

2

3

4

5

6

7

8

9

10

11

12

13

14

15

16

17

18

19

20

21

22

23

24

47

48

49

50

51

52

53

54

55

56

57

58 59

60

much longer time scale than the photochemical reaction generating the gas. As a consequence, the mechanical response is much slower and has it own kinetics, which is additionally affected by the ensuing release of gas. This work highlights the relevance of different intracrystalline forces that determine the mechanical effects as a result of release of gas molecules. These and other gas-releasing crystals could be of significant use to researchers looking to create single-crystalline machines, where the momentum generated by the gas propels a crystal as a macroscopic entity. These "crystalline machines" would represent the macroscopic versions of molecular and nanoscale robots that operate via gas-generating chemical reactions.

4. EXPERIMENTAL SECTION

4.1. Calculations. The geometries of all structures were optimized using the B3LYP level theory with a 6-31G+(d) basis set with Gaussian16 software.^{31,32,34} Absorption spectra of reactants, intermediates, and products were obtained using TD-DFT calculations using C-PCM solvation method and acetonitrile.^{35–37} Transition states were confirmed by analysis of one imaginary vibrational frequency as determined by the second derivative of the energy with respect to the optimized internal coordinates. The geometry of the transition state was also determined to be at a maximum of energy between the reactant and product by Internal Reaction Coordinate (IRC) calculations.^{38,39} All calculations were performed at the Ohio Supercomputer Center.

25 4.2. Laser Flash Photolysis. Laser flash photolysis in solution 26 and the solid-state were performed with a laser flash photolysis 27 apparatus connected to an excimer laser (308 nm, 17 ns).⁴⁰ The system at the University of Cincinnati is a commercial XE-LMP 28 Luzchem system using a Lambda Physik LPX 100 Excimer laser 29 at 308 nm with a 17 ns resolution. For solution laser flash 30 photolysis, stock solutions of derivatives 1a, 1b, and 1c in 31 acetonitrile were prepared with an absorption between 0.3 and 32 0.8 at 308 nm. Solid-state nanocrystalline suspensions are 33 prepared following the procedure by Simoncelli et al.³⁰ A 34 saturated acetone solution of 1a, 1b, or 1c was added to a water 35 solution in a volumetric flask placed in a ultrasound bath, until 36 the absorption at 308 nm was between 0.3 and 0.8. The samples 37 were placed in a quartz cuvette with a 10 mm x 10 mm cross 38 section, and for measurement obtained in argon- or oxygensaturated acetonitrile and suspentions, the cuvettes were capped 39 with rubber septum and the appropiate gas bubbled through 40 them for 5 minutes. Transient absorption spectra were produced 41 by plotting absorbance values that had been averaged from the 42 kinetic traces at 20 nm intervals from 300 to 600 nm over the 43 specified time intervals. Kinetic information was determined by 44 plotting averaged kinetic profiles from specified wavenlength 45 and fitting the kinetic profiles with Igor Pro data software 46 produced by WaveMetrics.

4.3. Preparation of starting materials

4.3.1. Synthesis of 1-phenyl-prop-2-yn-1-ol. We followed the procedure reported in the literature by Chassaing *et al.* and Pigge *et al.* with some modifications.^{41,42} To a solution of benzaldehyde (2.05 g 18.9 mmol) in 25 mL of anhydrous THF at 0°C was added a solution of ethynylmagnesium bromide (48 mL 24 mmol, 1.2 eq) in 15 mL of anhydrous THF. The mixture was stirred for 20 hours at 0°C and the reaction quenched by adding NH₄Cl (30 g of NH₄Cl dissolved in 100 mL of H₂O) and the resulting mixture was stirred for 1 hour. The solvent was

removed under vacuum and the residue extracted with diethyl ether (100 mL). The diethyl ether layer was washed twice with water, once with brine (saturated NaCl) and dried over anhydrous MgSO₄. The diethyl ether was evaporated under vacuum to yield crude 1-phenyl-prop-2-yn-1-ol (2.0 g, 15.2 mmol, 78% yield). ¹H NMR, ¹³C NMR and IR spectra of the product are consistent with those reported.⁴¹ ⁻¹H NMR (400 MHz, CDCl₃,): δ 2.38 (broad, 1H), 2.67 (d, J = 2.4 Hz, 1H), 5.46 (d, J = 2.4 Hz, 1H), 7.32 – 7.41 (m, 3H), 7.55 (d, J = 7.2 Hz, 2H) ppm; ¹³C NMR (100 MHz, CDCl₃): δ 64.4, 74.9, 83.5, 126.6, 128.6, 128.7, 140.0 ppm; IR (CDCl₃): δ 291, 3064, 3033, 2118, 1493, 1455, 1022, 1002, 947, 916, 698, 650 cm⁻¹.

4.3.2. Synthesis of 1-(4-methoxy-phenyl)-prop-2-yn-1-ol. The same procedure was followed for the synthesis of 1-phenyl-prop-2-yn-1-ol.^{41,42} A reaction of p-methoxybenzaldehyde (2.65 g, 19.5 mmol) with ethynylmagnesium bromide (48 mL, 24 mmol, 1.2 eq) resulted in 4-methoxy-phenyl)-prop-2-yn-1-ol (2a) (2.73 g, 16.8 mmol) in 86% yield. The ¹H NMR, ¹³C NMR and IR spectra of the product compare well with those in the literature.^{43,44} ¹H NMR (400 MHz, CDCl₃): δ 2.49 (broad, 1H), 2.66 (d, J = 2 Hz, 1H), 3.80 (s, 3H), 5.40 (d, J = 2 Hz, 1H), 6.90 (d, J = 8.4 Hz, 2H), 7.46 (d, J = 8.4 Hz, 2H) ppm.; ¹³C NMR (100 MHz, CDCl₃): δ 55.4, 64.0, 74.6, 83.8, 114.0, 128.1, 132.4, 159.8 ppm.; IR (CDCl₃): 3397, 3288, 3005, 2959, 2838, 2116, 1611, 1588, 1512, 1250, 1175, 1112, 1031, 913, 833 cm⁻¹.

4.3.3. Synthesis of 1-(4-chloro-phenyl)-prop-2-yn-1-ol. 1-Phenyl-prop-2-yn-1-ol was prepared in a similar manner as described above.^{41,42} A reaction of p-chlorobenzaldehyde (1.50 g, 10.7 mmol) with ethynylmagnesium bromide (48 mL, 24 mmol, 1.2 eq) resulted in 4 chloro-phenyl)-prop-2-yn-1-ol (1.7 g, 10.3 mml) in 96% yield. The NMR spectra of this compound were similar to previous literature values.⁴⁵ ¹H NMR (400 MHz, CDCl₃): δ 2.45 (broad, 1H), 2.66 (d, J = 2.0 Hz, 1H), 5. 40 (d, J = 2.0 Hz, 1H), 7.32 (d, J = 7.6 Hz, 2H), 7.46 (d, J = 7.6 Hz, 2H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ 1.8, 75.0, 82.3, 128.8, 132.8, 132.8, 137.3 ppm. IR (CDCl₃): δ 2.95, 818, 757, 645 cm⁻¹. GC/MS (EI): m/z 168, 167, 166, 149, 139, 131 (100), 113, 103, 77, 65.

4.3.4. Synthesis of 1-phenyl-propynone. 1-Phenylpropyone was prepared using a similar method to Pigge et al. with some modification.⁴² Jones reagent was prepared by mixing CrO₃ (4 g, 0.04 mol) with 4 mL of conc. H₂SO₄ to yield a slurry, to which water (3 x 4 mL) was added.²⁶ The Jones reagent was added dropwise to 1-phenyl-prop-2-yn-1-ol (2.0 g, 15.2 mmol) dissolved in acetone (25 mL) at 0°C, over a period of 10 min until the color of the solution changed to green and then to orange. The mixture was stirred for 30 min and the solvent removed under vacuum. The resulting residue was extracted with diethyl ether (100 mL). The ether layer was washed twice with water (100 mL), once with saturated NaHCO₃ (100 mL), once with saturated brine solution (100 mL), and dried over anhydrous MgSO₄. The diethyl ether was evaporated under vacuum to yield crude 1-phenyl-propynone (1.38 g, 10.6 mmol) 70% yields. ¹H NMR, ¹³C NMR and IR spectra of this compound correspond with the literature.^{46,47} ¹H NMR (400 MHz, CDCl₃): δ 3.45 (s, 1H), 7.51 (t, J = 7.8 Hz, 2H), 7.66 (t, J = 7.4 Hz, 1H), 8.18 (d, J = 8.4 Hz, 2H) ppm.; ${}^{13}C$ NMR (100 MHz, CDCl₃): δ 80.3, 80.8, 128.7, 129.7, 134.5, 136.2, 177.4 ppm; IR (CDCl₃): 3237, 2094, 1638, 1264, 1072, 1072, 1031, 696 cm⁻¹.

4.3.5. Synthesis of 1-(4-methoxy-phenyl)-propynone. 1-(4-Methoxy-phenyl)-prop-2-yn-1-ol (2.74 g, 16.8 mmol) was used

as described above⁴² to produce crude 1-(4-methoxy-phenyl)propynone (2.01 g, 12.5 mmol) in 74% yields. ¹H NMR, ¹³C NMR and IR of this compound agree with those reported previously.^{46–48} ¹H NMR (400 MHz, CDCl₃): δ 3.34 (s, 1H), 3.90 (s, 3H), 6.97 (d, J = 8.8 Hz, 2H), 8.14 (d, J = 8.8 Hz, 2H) ppm; ¹³C NMR (100 MHz, CDCl₃): δ 55.6, 80.0, 80.4, 114.0, 129.6, 132.2, 164.8, 176.0 ppm; IR (CDCl₃): 3251, 2991, 2093, 1640, 1599, 1024, 840, 686 cm⁻¹.

1

2

3

4

5

6

7

8

9

10

11

12

13

14

15

16

17

59

60

4.3.6. Synthesis of 1-(4-chloro-phenyl)-propynone. 1-(4-Chloro-phenyl)-propynone (1.7 g, 10.3 mmol) was used as described above⁴² to produce crude 1-(4-methoxy-phenyl)-prop-2-yn-1-ol (1.46 g, 8.9 mmol) in 86% yields. The NMR spectra of this compound were similar to those reported.^{47–50} ¹H NMR (CDCl₃, 400 MHz): δ 3.46 (s, 1H), 7.49 (d, J = 8 Hz, 2H), 8.10 (d, J = 8 Hz, 2H) ppm; ¹³C NMR (100 MHz, CDCl₃): δ 81.2, 81.3, 131.8, 133.4, 133.9, 134.5, 175.9 ppm; IR (CDCl₃): 3225, 2088, 1652, 1588, 1564, 1462, 1432, 1235, 1136, 1040, 999, 730, 675, 626 cm⁻¹; GC/MS (EI): m/z 166, 165, 164, 139, 138, 137, 136 (100), 111, 101, 85, 75.

18 4.3.7. Synthesis of 3,3-dibromo-1-phenyl-propan-1-one. 3,3-19 Dibromo-1-phenyl-propan-1-one was synthesized following the 20 procedure reported by Sanseverino et al. with some 21 modifications.⁴⁹ 1-Phenyl-propynone (1.38 g, 10.6 mmol) was dissolved in dichloromethane (25 mL) and kept at -8°C and SiO₂ 22 (6.36 g, 106 mmol, 10 eq) added, followed by dropwise addition 23 of PBr₃ (1.924 g, 7.1 mmol, 0.66 eq) in dichloromethane (10 24 mL) using a dropping funnel over a period of 10 min. The 25 mixture was stirred for 20 hours and the SiO₂ was filtered off 26 and the solution dried. The solvent was removed under vacuum 27 to yield crude 3,3-dibromo-1-phenyl-propan-1-one (2.82 g, 9.6 28 mmol, 91% yield). The product was characterized using ¹H 29 NMR, ¹³C NMR, IR and MS spectroscopy. The NMR and IR 30 spectra are consistent with literature values.⁵⁰ ¹H NMR (400 MHz, CDCl₃): δ 4.19 (d, J = 6.7 Hz, 2H), 6.20 (t, J = 6.7 Hz, 31 1H), 7.51 (t, J = 7.6 Hz, 2H), 7.63 (t, J = 7.4 Hz, 1H), 7.96 (d, J 32 = 7.6 Hz, 2H) ppm; ¹³C NMR (100 MHz, CDCl₃): δ 36.7, 53.3, 33 128.2, 128.9, 134.0, 135.7, 194.3 ppm. IR (CDCl₃): 1684, 1598, 34 1580, 1347, 1263, 1219, 755, cm⁻¹; HRMS: m/z calculated for 35 $C_9H_8O_2Br_2Na^+$ [M+Na]⁺, 314.8819; found, 314.8738; m/z 36 calculated for $C_9H_8O_2Br_2H^+$ [M+H]⁺, 292.9000; found, 37 292.9025. 38

4.3.8. Synthesis of 3,3-dibromo-1-(4-methoxy-phenyl)-propan-39 1-one. Synthesis of 3,3-dibromo-1-(phenyl)-propan-1-one was 40 accomplished by a similarly modified Sanseverino procedure as 41 described above.⁴⁹ A reaction of 1-(4-methoxy-phenyl)-42 propynone (2.01 g, 12.5 mmol) resulted in crude 3,3-dibromo-43 1-(4-methoxy-phenyl)-propan-1-one (3.54 g, 11.0 mmol, 88% 44 yield). The product was characterized using ¹H NMR, ¹³C NMR, 45 IR and MS spectroscopy. ¹H NMR (400 MHz, CDCl₃): δ 3.89 (s, 3H), 4.13 (d, J = 6.4 Hz, 2H), 6.19 (t, J = 6.4 Hz, 1H), 6.97 46 (d, J = 8.8 Hz, 2H), 7.94 (d, J = 8.8 Hz, 2H) ppm; 13 C NMR 47 (CDCl₃, 100 MHz): δ 37.3, 52.9, 55.6, 114.1, 128.8, 130.7, 48 164.2, 192.8 ppm; IR: 1673, 1599, 1574, 1463, 1421, 1398, 49 1346, 1318, 1311, 1258, 1223, 785, cm⁻¹; HRMS: m/z calculated 50 for C₁₀H₁₀O₂Br₂Na⁺ [M+Na]⁺, 344.89193; found, 344.89206. 51

524.3.9. Synthesis of 3,3-dibromo-1-(4-chloro-phenyl)-propan-1-
one. We followed the same procedure as for synthesis of 3,3-
dibromo-1-(phenyl)-propan-1-one. 49 A reaction of 1-(4-
methoxy-phenyl)-propynone (2.01 g, 12.5 mmol) resulted in
crude 3,3-dibromo-1-(4-chloro-phenyl)-propan-1-one (2.0 g,
6.1 mmol, 69% yield). ¹H NMR (400 MHz, CDCl₃): δ 4.19 (d, J
= 6.8 Hz, 1H), 6.17 (t, J = 6.8 Hz, 1H), 7.48 (d, J = 7.8 Hz, 2H)58

7.99 (d, J = 7.8 Hz, 2H) ppm; ¹³C NMR (100 MHz, CDCl₃): δ 36.3, 57.3, 129.8, 130.8, 132.8, 137.6, 197.0 ppm; IR (CDCl₃): 1693, 1588, 1569, 1468, 1432, 1344, 1270, 1213, 1073, 1040, 979, 757, 626, 584 cm⁻¹; GC/MS (EI): m/z 248, 246, 244, 218, 165, 139 (100), 133, 111, 105, 85, 75. RMS: *m/z* calculated for C₉H₇ONaClBr₂ [M+Na]⁺, 346.8450; found, 346.8452.

4.3.10. Synthesis of 3-azido-1-phenyl-propenone (1a). 3,3-Dibromo-1-phenyl-propan-1-one (1.69 g, 5.8 mmol) was dissolved in 20 mL of methanol and 20 mL of acetone at 0°C. NaN₃ (1.01 g, 15.5 mmol, 5 eq) dissolved in a minimal amount of water (~5 mL) was added to the solution. The mixture was stirred for ~1 hour. The solvent was removed under vacuum and the resulting residue was extracted with diethyl ether (50 mL). The ether layer was washed twice with water (100 mL), once saturated brine (100 mL), and dried over anhydrous MgSO₄. The solvent was evaporated under vacuum to give crude 3-azido-1phenyl-propenone (1a) (0.710 g, 4.1 mmol, 71% yields). The crude was recrystallized from dichloromethane to give pale yellow crystals. The product was characterized using ¹H NMR, ¹³C NMR, IR, and MS spectroscopy. mp (observed): 78 – 84°C $(\text{lit.}^{51} 87 - 87.5^{\circ}\text{C})$. ¹H NMR (400 MHz, CDCl₃): δ 6.77 (d, J = 13.2 Hz, 1H), 7.48 (t, J = 7.6 Hz, 2H), 7.50 (d, J = 13.2Hz, 1H), 7.58 (t, J = 7.4 Hz, 1H), 7.92 (d, J = 7.2 Hz, 2H) ppm; ¹³C NMR (100 MHz, CDCl₃): 8 113.2, 128.2, 128.7, 133.0, 137.7, 144.9, 188.8 ppm; IR: 3069, 2133, 1657, 1596, 1575, 1448, 1253, 1215, 1018, 950, 773, 682, 644 cm⁻¹. HRMS: m/z calculated for C₉H₇N₃ONa⁺ [M+Na]⁺, 196.04813; found, 196.04816.

4.3.11. Synthesis of 3-azido-1-(4-methoxy-phenyl)-propenone (1b). The synthesis for 1b was analogous to 1a. 3,3-Dibromo-1-(4-methoxy-phenyl)-propan-1-one (1.43 g, 4.4 mmol) resulted in crude 3-azido-1-(4-methoxy-phenyl)-propenone (1b) (0.790 g, 3.9 mmol, 88% yields). The crude was recrystallized from dichloromethane and yielded pale-yellow crystals which were characterized using ¹H NMR, ¹³C NMR, IR and MS spectroscopy. mp (observed): 105-108°C (lit.;⁵¹ 109-110°C). ¹H NMR (400 MHz, CDCl₃): δ 3.88 (s, 3H), 6.76 (d, J = 13 Hz, 1H), 6.95 (d, J = 8.8 Hz, 2H), 7.48 (d, J = 13 Hz, 1H), 7.92 (d, J = 8.8 Hz, 2H) ppm; ¹³C NMR (100 MHz, CDCl₃): δ 55.5, 113.0, 113.9, 130.6, 144.0, 163.6, 187.1 ppm; IR: 3045, 2138, 1658, 1592, 1574, 1515, 1256, 1226, 1172, 1024, 954, 822, 779, 599 cm⁻¹. HRMS: *m/z* calculated for C₁₀H₉N₃O₂Na⁺ [M+Na]⁺, 226.05870; found, 226.05873.

4.3.12. Synthesis of 3-azido-1-(4-chloro-phenyl)-propenone (1c). The synthesis of 1c was similar to that described for 1a. 3,3-Dibromo-1-(4-chloro-phenyl)-propan-1-one (2.0 g, 6.1 mmol) resulted in crude 3-azido-1-(4-chloro-phenyl)-propenone (1c) (0.68 g, 5.4 mmol) in 89% yield. mp (observed): 93-98°C (lit.;⁵¹ 98-99°C). ¹H NMR (400 MHz, CDCl₃): δ 6.37 (d, J = 14 Hz, 1H), 7.47 (d, J = 8.8 Hz, 2H) 7. 53 (d, J = 14 Hz, 1H), 7.86 (d, J = 8.8 Hz, 2H) pm; ¹³C NMR (100 MHz, CDCl₃): δ 117.5, 129.6, 131.2, 136.0, 139.5, 145.4, 187.4 ppm; IR: 3051, 2126, 1660, 1590, 1568, 1254, 1213, 1091, 1013, 823 cm⁻¹; GC/MS (EI): m/z 181, 180, 179, 151, 141, 140, 139, 126, 125, 124, 116, 113, 112, 111, 89, 85, 75, 68, 64.

4.4. Photolytic studies

4.4.1. Photolysis of **1a** in chloroform-d. A solution of **1a** (14 mg, 0.08 mmol) in CDCl₃ (1 mL) was purged with argon for 5 min and photolyzed via a Pyrex filter for up to 24 hours at 298 K. ¹H NMR and GC analysis of the reaction mixture showed the formation of **3a**, **4a** and **5a**. The products were characterized by GC-MS chromatography, ¹H-NMR, ¹³C-NMR and IR spectroscopy of the reaction mixture. The spectral data of **4a** and

2

3

4

5

6

7

8

9

58 59

60

5a match with those reported in the literature.^{21–25} 2-Phenyl-2Hazirine (**3a**): ¹H NMR (400 MHz, CDCl₃,): δ 3.47 (d, J = 2 Hz, 1H), 7.44 – 7.55 (m, 3H), 8.06 (d, J = 8.4 Hz, 2H), 9.57 (d, J = 2 Hz, 1H) ppm; ¹³C NMR (100 MHz, CDCl₃): δ 28.4, 128.3, 128.8, 133.6, 136.9, 152.4, 197.4 ppm; 5-Phenyl-1,2-oxazole (4a): ¹H NMR (400 MHz, CDCl₃): δ 6.53 (d, J = 1.6 Hz, 1H), 7.44 - 7.55 (m, 2H), 7.61 - 7.69 (m, 1H), 7.79 - 7.82 (m, 2H), 8.30 (d, J = 1.6 Hz, 1H) ppm; ¹³C NMR (100 MHz, CDCl₃): δ 98.7, 125.9, 127.3, 129.0, 130.2, 150.9, 169.4 ppm; 3-Oxo-3phenylpropanenitrile (5a): ¹H NMR (400 MHz, CDCl₃): δ 4.10 (s, 2H), 7.53 (t, J = 7.2 Hz, 2H), 7.67 (t, J = 7.2 Hz, 1H), 7.93 (d, J = 7.2 Hz), 7.93 (d, J =10 J = 7.2 Hz, 2H) ppm; ¹³C NMR (100 MHz, CDCl₃): δ 29.4, 11 113.8, 128.5, 129.2, 134.3, 134.8, 187.1 ppm. IR (CDCl₃): 2263, 12 1689 cm⁻¹.

13 4.4.2. Photolysis of 1b in chloroform-d. A solution of 1b (20 14 mg, 0.1 mmol) in CDCl₃ (1 mL) was purged with argon for 5 15 min and photolyzed via a Pyrex filter for up to 24 hours at 298 16 K. GC and NMR analysis of the reaction mixture showed the 17 formation of 3b, 4b and 5b. The products were characterized by 18 GC-MS chromatography, 1H-NMR, 13C-NMR and IR 19 spectroscopy of the reaction mixture. The spectral data for 4b 20 and 5b match with those reported in the literature.²¹⁻²⁵ 2-(4-Methoxy-phenyl)-2H-azirine (3b): ¹H NMR (400 MHz, CDCl₃): 21 δ 3.43 (d, J = 2.0 Hz, 1H), 3.86 – 3.89 (m, 3H), 6.97 – 7.00 (m, 22 2H), 8.057 (d, J = 8.8 Hz), 9.57 (d, J = 2.0 Hz, 1H) ppm; ^{13}C 23 NMR (100 MHz, CDCl₃): δ 28.0, 55.5, 114.0, 130.0, 130.6, 24 152.9, 163.9, 195.6 ppm. IR (CDCl₃): 1663 cm⁻¹. 5-(4-Methoxy-25 phenyl)-1,2-oxazole (4b): ¹H NMR (400 MHz, CDCl₃): δ 3.86 26 (s, 3H), 6.40 (d, J = 1.6 Hz, 1H), 6.97 - 7.00 (m, 2H), 7.74 (d, J)27 = 8.8 Hz, 2H), 8.25 (d, J = 2.0 Hz, 1H) ppm; ¹³C NMR (100) 28 MHz, CDCl₃): δ 55.4, 97.3, 114.4, 120.2, 127.5, 150.8, 161.1, 29 169.3 ppm.; IR (CDCl₃): 3014, 2946, 2840, 1599, 1462, 826 cm⁻ 30 ¹; GC/MS (EI): m/z 175 (M, 100%), 160, 135, 120, 107, 92, 77, 31 63, 51. 3-Oxo-3-(4-methoxy-phenyl) propanenitrile (5b): ¹H 32 NMR (400 MHz, CDCl₃): δ 3.90 (s, 3H), 4.03 (s, 2H), 6.98 (d, 33 J = 8.8 Hz, 2H, 7.90 (d, J = 8.8 Hz, 2H) ppm; ¹³C NMR (CDCl₃, 34 100 MHz): 8 29.0, 55.7, 114.1, 114.3, 127.5, 130.9, 164.7, 185.4 35 ppm. IR (CDCl₃): 2260, 1682 cm⁻¹.

36 4.4.3. Photolysis of 1c in chloroform-d. A solution of 1c in 37 CDCl₃ was purged with argon for 5 min and photolyzed via a 38 Pyrex filter for up to 24 hours at 298 K. GC analysis of the reaction mixture showed the formation of 3c, 4c and 5c. The 39 products were characterized 1H-NMR, 13C-NMR and IR 40 spectroscopy of the reaction mixture. The spectral data for 4c 41 and 5c match with those reported in the literature. ²¹⁻²⁵ 2-(4-42 Chloro-phenyl)-2H-azirine (3c): ¹H NMR (400 MHz, CDCl₃): δ 43 3.42 (d, J = 2.4 Hz, 1H), 7.44 – 7.54 (m, 2H), 7.87 (d, J = 8.4 44 Hz, 2H), 9.56 (d, J = 2.0 Hz, 1H) ppm; ¹³C NMR (100 MHz, 45 CDCl₃): 28.3, 129.8, 131.5, 135.1, 140.1, 152.2, 196.2 ppm. 5-46 (4-Chloro-phenyl)-1,2-oxazole (4c): ¹H NMR (400 MHz, 47 CDCl₃): 8 6.52 (d, J = 2 Hz, 1H), 7.46 (d, J = 8.4, 2H), 7.74 (d, 48 J = 8.4, 2H, 8.30 (d, J = 1.6 Hz, 1H) ppm; ¹³C NMR (100 MHz, 49 CDCl₃): 8 99.0, 125.7, 127.2, 129.3, 136.3, 150.9, 168.3 ppm. 3-50 Oxo-3-(4-chloro-phenyl)propanenitrile (5c): ¹H NMR (400 51 MHz, CDCl₃): δ 4.06 (s, 2H), 7.51 (d, J = 8.4 Hz, 2H), 7.87 (d, 52 J = 8.4 Hz, 2H) ppm; ¹³C NMR (100 MHz, CDCl₃); δ 29.4. 113.4, 129.7, 129.9, 132.5, 141.5, 186.0 ppm. 53

54 4.4.4. Solid-State Photolysis of vinyl azides 1a-1c. Crystals of each vinyl azide (5-10 mg) were crushed between two 55 microscope slides and exposed to either a mercury arc lamp in 56 Pyrex or 400 nm LED for 1 h and the sample was analyzed by 57

¹H-NMR and IR spectroscopy. In each case, the photoproduct formed was the corresponding azirine 3.

4. 5. Thermolysis of vinyl azides 1a-1c. NMR tubes were charged with solutions of **1a-1c** (4.0 mg) in CDCl₃ (0.5 mL). The NMR tubes were heated in a pre-heated oil bath at 70°C for 10 min. ¹H NMR, ¹³C-NMR, and IR spectroscopy of the reaction mixture showed the formation of the corresponding azirines 3 and cyanides 5.

4.6. Nanoindentation. The nanoindentation measurements on **1b** and **1c** were performed with an Agilent G200 nanoindenter equipped with an XP head, using Berkovitch diamond indenter. Each indentation was performed using the continuous stiffness method to a depth of 1000 nm with a strain rate of 0.05, an amplitude of 2 nm, and a frequency of 45 Hz.52 Prior to the indentation, the stiffness and the geometry of the tip were determined by using Corning 7980 silica reference sample (Nanomechanics S1495-25). In order to ensure that the tip was fully engaged, the modulus was measured between 200 and 1000 nm. The value of the Poisson's ratio was assumed to be 0.30. A comparison of the young's modulus of 1b and 1c crystals with a very few relevant recent photoresponsive systems were provided in Supporting Information Table S10.53-54

4.7. Crystal Movement Video Specifications. Crystals of vinyl azides 1a, 1b, and 1c were grown from a dichloromethane solution at 0°C and placed on the stage of a Keyence VHX-1000E digital microscope. The photolysis was initiated using a LuzChem LED array with blue light, as well as two LED's of 365 nm and 400 nm outputs. The photolysis was recorded over the course of a few min of exposure for video 2-8 and 60 min for video 1.

ASSOCIATED CONTENT

The Supporting Information is available free of charge on the ACS Publications website. https://pubs.acs.org/doi/10.1021/

Spectra for characterization of **1a-c** and the photoproducts; DFT calculation data; CCDC 2015372-2015374 which contain the crystallographic data in CIF format. These data can be obtained, free of charge via http://www.ccdc.cam.ac.uk/products/csd/request/ (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, U.K.; Fax: 44-1223-336033 or e-mail: deposit@ccdc.cam.ac.uk).

AUTHOR INFORMATION

Corresponding Authors

Anna D. Gudmundsdottir – Department of Chemistry, University of Cincinnati, Cincinnati, OH 45221-0172, United States; Email: anna.gudmundsdottir@uc.edu

Panče Naumov - New York University Abu Dhabi, P. O. Box 129188, Abu Dhabi, United Arab Emirates; Email: pance.naumov@nyu.edu

Authors

Dylan J. Shields – Department of Chemistry, University of Cincinnati, Cincinnati, OH 45221-0172, United States;

Durga Prasad Karothu – New York University Abu Dhabi, P. O. Box 129188, Abu Dhabi, United Arab Emirates

Karthik Sambath– Department of Chemistry, University of Cincinnati, Cincinnati, OH 45221-0172, United State

Ranaweera A. A. Upul Ranaweera – Department of Chemistry, University of Cincinnati, Cincinnati, OH 45221-0172, United States

Stefan Schramm[†] – New York University Abu Dhabi, P. O. Box 129188, Abu Dhabi, United Arab Emirates

Alexander Duncan – Department of Chemistry, University of Cincinnati, Cincinnati, OH 45221-0172, United States

Benjamin Duncan – Department of Chemistry, University of Cincinnati, Cincinnati, OH 45221-0172, United States

Jeanette A. Krause – Department of Chemistry, University of Cincinnati, Cincinnati, OH 45221-0172, United States

Present Addresses

†Present address: BASF SE, Carl-Bosch-Strasse 38, 67056 Ludwigshafen am Rhein, Germany

Author Contributions

[‡]KS and RAAUR contributed equally.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENT

We thank the NSF (CHE-1800140 & MRI:CHE-1726092) and OSC (PES0597) for their support. DJS acknowledges Doctoral Enhancement, Stecke, and Twitchell Fellowships; RAAUR acknowledges Harry B. Mark, Ann P. Villalobos, and URC Fellowships. Funding for the SMART6000 CCD diffractometer was through NSF-MRI grant CHE-0215950. Synchrotron X-ray data were collected through the SCrALS (Service Crystallography at Advanced Light Source) program at Beamline 11.3.1 at the Advanced Light Source (ALS), Lawrence Berkeley National Laboratory. The ALS is supported by the U.S. Department of Energy, Office of Energy Sciences Materials Sciences Division, under contract DE-AC02-05CH11231.

REFERENCES

- (1) Yu, Y.; Nakano, M.; Ikeda, T. Directed bending of a polymer film by light. *Nature* **2003**, *425*, 145–145.
- (2) Al-Kaysi, R. O.; Tong, F.; Al-Haidar, M.; Zhu, L.; Bardeen, C. J. Highly branched photomechanical crystals. *Chem. Commun.* 2017, *53*, 2622–2625.
- (3) Ikeda, T.; Mamiya, J.-i.; Yu, Y. Photomechanics of liquidcrystalline elastomers and other polymers. *Angew. Chem. Int. Ed.* 2007, 46, 506–528.
- (4) Juodkazis, S.; Mukai, N.; Wakaki, R.; Yamaguchi, A.; Matsuo, S.; Misawa, H. Reversible phase transitions in polymer gels induced by radiation forces. *Nature* 2000, 408, 178–181.
- (5) Commins, P.; Desta, I. T.; Karothu, D. P.; Panda, M. K.; Naumov, P. Crystals on the move: Mechanical effects in dynamic solids. *Chem. Commun.* 2016, *52*, 13941–13954.
- (6) Ahmed, E.; Karothu, D. P.; Naumov, P. Crystal adaptronics: Mechanically reconfigurable elastic and superelastic molecular crystals. *Angew. Chem., Int. Ed.* **2018**, *57*, 8837–8846.

- (7) Karothu, D. P.; Halabi, J. M.; Li, L.; Colin-Molina, A.; Rodríguez-Molina, B.; Naumov, P. Global performance indices for dynamic crystals as organic thermal actuators. *Adv. Mater.* 2020, *32*, 1906216.
- (8) Ahmed, E.; Karothu, D. P.; Warren, M.; Naumov, P. Shape memory effects in molecular crystals. *Nat. Commun.* 2019, 10, 3723.
- (9) Naumov, P.; Karothu, D. P.; Ahmed, E.; Catalano, L.; Commins, P.; Halabi, J. M.; Al-Handawi, M. B.; Li, L. The Rise of the Dynamic Crystals. J. Am. Chem. Soc. 2020, 142, 13256–13272.
- (10) Naumov, P.; Chizhik, S.; Panda, M. K.; Nath, N. K.; Boldyreva, E. Mechanically responsive molecular crystals. *Chem. Rev.* 2015, *115*, 12440–12490.
- (11) Naumov, P.; Sahoo, S. C.; Zakharov, B. A.; Boldyreva, E. V. Dynamic single crystals: Kinematic analysis of photoinduced crystal jumping (the photosalient effect). *Angew. Chem. Int. Ed.* **2013**, *52*, 9990–9995.
- (12) Ovcharenko, V. I.; Sagdeev, R. Z. Molecular ferromagnets. *Russ. Chem. Rev.*, **1999**, *68*, 345–363.
- (13) Ovcharenko, V. I.; Fokin, V. I.; Romanenko, G. V.; Korobkov, I. V.; Rey, P. Synthesis of vicinal bishydroxylamin. *Russ. Chem. Bull.* **1999**, *48*, 1519–1525.
- (14) Ovcharenko, V. I.; Fokin, S. V.; Fursova, E. Y.; Kuznetsova, O. V.; Tretyakov, E. V.; Romanenko, G. V.; Bogomyakov, A. S. "Jumping crystals": Oxygen-evolving metal-nitroxide complexes. *Inorg. Chem.* 2011, *50*, 4307–4312.
- (15) Chevilott, P. F.; Edwards, W. F. Ann. Chim. Phys., 1817, 4, 287.
- (16) Chevilott, P. F.; Edwards, W. F. Ann. Chim. Phys., 1818, 8, 333.
- (17) Boldyrev, V. V. Mechanochemical Processes with the Reaction-Induced Mechanical Activation. Chemo-Mechanochemical Effect. *Russ. Chem. Bull.* **2018**, *67*, 933–948.
- (18) Oates, W. A.; Todd, D. D. Proc. First Australian Conference on Electron Microscopy, Hobart, **1965**, page 88.
- (19) Bowden, F. P.; Yoffe, A. D. Fast Reactions in Solids. *Angew. Chem.* **1959**, *71*, 752.
- (20) Sato, S. Azirines. IV. The photolysis of β-azidovinyl ketones. Bull. Chem. Soc. Jpn. 1968, 41, 2524–2525.
- (21) Rosa, F. A.; Machado, B.; Bonacorso, H. G.; Zanatta, N.; Martins, M. A. P. Reaction of β-dimethylaminovinyl ketones with hydroxylamine: A simple and useful method for synthesis of 3and 5-substituted isoxazoles. *J. Heterocycl. Chem.* **2008**, *45*, 879– 885.
- (22) Isomura, K.; Hirose, Y.; Shuyama, H.; Abe, S.; Ayabe, G.-i; Taniguchi, H. Unusual formation of oxazoles by base- or acidcatalyzed ring opening of 2-acyl-2*H*-azirines. *Heterocycl.* **1978**, *9*, 1207–1216.
- (23) James, M. L.; Fulton, R. R.; Henderson, D. J.; Eberl, S.; Meikle, S. R.; Thomson, S.; Allan, R. D.; Dolle, F.; Fulham, M. J.; Kassiou, M. Synthesis and *in vivo* evaluation of a novel peripheral benzodiazepine receptor PET radioligand. *Bioorg. Med. Chem.* 2005, *13*, 6188–6194.
- (24) Gøgsig, T. M.; Nielsen, D. U.; Lindhardt, A. T.; Skrydstrup, T. Palladium catalyzed carbonylative Heck reaction affording monoprotected 1,3-ketoaldehydes. *Org. Lett.* **2012**, *14*, 2536– 2539.
- (25) Shen, J.; Yang, D.; Liu, Y.; Qin, S.; Zhang, J.; Sun, J.; Liu, C.; Liu, C.; Zhao, X.; Chu, C.; Liu, R. Copper-catalyzed aerobic oxidative coupling of aromatic alcohols and acetonitrile to β-ketonitriles. *Org. Lett.* **2014**, *16*, 350–353.
- (26) Nesmeyanov, A. N.; Rybinskaya, M. I.; Kelekhsaeva, T. G. Effect of stereochemical and electronic factors on the decomposition and rearrangement of β-azidovinyl ketones. *Bull. Acad. Sci. USSR, Div. Chem. Sci.* **1969**, *18*, 787–790.
- (27) Hirshfeld, F. L.; Schmidt, G. M. J. Topochemical control of solidstate polymerization. J. Polym. Sci., Part A 1964, 2, 2181–2190.
- (28) Sarkar, S. K.; Sawai, A.; Kanahara, K.; Wentrup, C.; Abe, M.; Gudmundsdottir, A. D. Direct detection of a triplet vinylnitrene, 1,4-naphthoquinone-2-ylnitrene, in solution and cryogenic matrices. J. Am. Chem. Soc. 2015, 137, 4207–4214.
- (29) Rajam, S.; Murthy, R. S.; Jadhav, A. V.; Li, Q.; Keller, C.; Carra, C.; Pace, T. C. S.; Bohne, C.; Ault, B. S.; Gudmundsdottir, A. D.

2

3

Photolysis of (3-methyl-2*H*-azirin-2-yl)-phenylmethanone: Direct detection of a triplet vinylnitrene intermediate. *J. Org. Chem.* **2011**, *76*, 9934–9945.

- (30) Simoncelli, S.; Kuzmanich, G.; Gard, M. N.; Garcia-Garibay, M. A. Photochemical reaction mechanisms and kinetics with molecular nanocrystals: Surface quenching of triplet benzophenone nanocrystals. J. Phys. Org. Chem. 2010, 23, 376–381.
- (31) Becke, A. D. Density-functional thermochemistry. III. The role of exact exchange. J. Chem. Phys. 1993, 98, 5648–5652.
- (32) Lee, C.; Yang, W.; Parr, R. G. Development of the Colle-Salvetti correlation-energy formula into a functional of the electron density. *Phys. Rev. B* 1988, *37*, 785–789.
- (33) Mackenzie, C. F.; Spackman, P. R.; Jayatilaka, D.; Spackman, M. A. *CrystalExplorer* model energies and energy frameworks: Extension to metal coordination compounds, organic salts, solvates and open-shell systems. *IUCrJ* 2017, *4*, 575–587.
- (34) Gaussian 16, Revision C.01, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Petersson, G. A.; Nakatsuji, H.; Li, X.; Caricato, M.; Marenich, A. V.; Bloino, J.; Janesko, B. G.; Gomperts, R.; Mennucci, B.; Hratchian, H. P.; Ortiz, J. V.; Izmaylov, A. F.; Sonnenberg, J. L.; Williams-Young, D.; Ding, F.; Lipparini, F.; Egidi, F.; Goings, J.; Peng, B.; Petrone, A.; Henderson, T.; Ranasinghe, D.; Zakrzewski, V. G.; Gao, J.; Rega, N.; Zheng, G.; Liang, W.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Throssell, K.; Montgomery, J. A., Jr.; Peralta, J. E.; Ogliaro, F.; Bearpark, M. J.; Heyd, J. J.; Brothers, E. N.; Kudin, K. N.; Staroverov, V. N.; Keith, T. A.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A. P.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Millam, J. M.; Klene, M.; Adamo, C.; Cammi, R.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Farkas, O.; Foresman, J. B.; Fox, D. J. Gaussian, Inc., Wallingford CT, 2016.
 - (35) Foresman, J. B.; Head-Gordon, M.; Pople, J. A.; Frisch, M. J. Toward a systematic molecular orbital theory for excited states. *J. Phys. Chem.* **1992**, *96*, 135–149.
 - (36) Bauernschmitt, R.; Ahlrichs, R. Treatment of electronic excitations within the adiabatic approximation of time dependent density functional theory. *Chem. Phys. Lett.* **1996**, *256*, 454–464.
 - (37) Mennucci, B.; Tomasi, J.; Cammi, R.; Cheeseman, J. R.; Frisch, M. J.; Devlin, F. J.; Gabriel, S.; Stephens P. J. Polarizable continuum model (PCM) calculations of solvent effects on optical rotations of chiral molecules. *J. Phys.C hem.* A 2002, *106*, 6102– 6113.
 - (38) Gonzalez, C.; Schlegel, H. B. Reaction path following in massweighted internal coordinates *J. Phys. Chem.* **1990**, *94*, 5523– 5527.
 - (39) Gonzalez, C.; Schlegel, H. B. J. An improved algorithm for reaction path following. *Chem. Phys.* **1989**, *90*, 2154–2161.
 - (40) Muthukrishnan, S.; Sankaranarayanan, J.; Klima, R. F.; Pace, T. C. S.; Bohne, C.; Gudmundsdottir, A. D. Intramolecular H-atom abstraction in γ-azido-butyrophenones: Formation of 1,5 ketyl iminyl radicals. *Org. Lett.* **2009**, *11*, 2345–2348.
 - (41) Chassaing, S.; Kueny-Stotz, M.; Isorez, G.; Brouillard, R. Rapid preparation of 3-deoxyanthocyanidins and novel dicationic

derivatives: New insight into an old procedure. *Eur. J. Org. Chem.* **2007**, 2438–2448.

- (42) Pigge, F. C.; Ghasedi, F.; Zheng, Z.; Rath, N. P.; Nichols, G.; Chickos, J. S. Structural characterization of crystalline inclusion complexes formed from 1,3,5-triaroylbenzene derivatives-a new family of inclusion hosts. *J. Chem. Soc., Perkin Trans.* 2, 2000, 2458–2464.
- (43) Park, S.; Joo, J. M.; Cho, E. J. Synthesis of β-trifluoromethylated ketones from propargylic alcohols by visible light photoredox catalysis. *Eur. J. Org. Chem.* **2015**, 4093–4097.
- (44) Kalhor-Monfared, S.; Beauvineau, C.; Scherman, D.; Girard, C. Synthesis and cytotoxicity evaluation of aryl triazolic derivatives and their hydroxymethine homologues against B16 melanoma cell line. *Eur. J. Med.* **2016**, *122*, 436–441.
- (45) Maeda, Y.; Kakiuchi, N.; Matsumura, S.; Nishimura, T.; Kawamura, T.; Uemura, S. Oxovanadium complex-catalyzed aerobic oxidation of propargylic alcohols. *J. Org. Chem.* 2002, 67, 6718–6724.
- (46) Zheng, M.; Wu, F.; Chen, K.; Zhu, S. Styrene as 4π-component in Zn(II)-catalyzed intermolecular Diels–Alder/Ene tandem reaction. Org. Lett. 2016, 18, 3554–3557.
- (47) Weerasiri, K. C.; Gorden, A. E. V. Oxidation of propargylic alcohols with a 2-quinoxalinol salen copper(II) complex and tertbutyl hydroperoxide. *Eur. J. Org. Chem.* **2013**, 1546–1550.
- (48) Shi, F.; Luo, S.-W.; Tao, Z.-L.; He, L.; Yu, J.; Tu, S.-J.; Gong, L.-Z. The catalytic asymmetric 1,3-dipolar cycloaddition of ynones with azomethine ylides. *Org. Lett.* **2011**, *13*, 4680–4683.
- (49) Sanseverino, A. M.; de Mattos, M. C. S. Hydrobromination of alkenes with PBr₃/SiO₂: A simple and efficient regiospecific preparation of alkyl bromides. *J. Braz. Chem. Soc.* **2001**, *12*, 685– 687.
- (50) Pirtsch, M.; Paria, S.; Matsuno, T.; Isobe, H.; Reiser, O. [Cu(dap)₂Cl] as an efficient visible-light-driven photoredox catalyst in carbon–carbon bond-forming reactions. *Chem. Eur. J* 2012, *18*, 7336–7340.
- (51) Fischer, G. W. Vinyloge acylverbindungen, VII. Synthese und reaktives verhalten vinyloger *N*-Acyl-pyridiniumsalze. *Chem. Ber.* **1970**, *103*, 3470–3488.
- (52) Oliver, W. C.; Pharr, G. M. An improved technique for determining hardness and elastic modulus using load and displacement sensing indentation experiments. *J. Mater. Res.* 1992, 7, 1564–1583.
- (53) Annadhasan, M.; Karothu, D. P.; Chinnasamy, R.; Catalano, L.; Ahmed, E.; Ghosh, S.; Naumov, P.; Chandrasekar, R. Micromanipulation of mechanically compliant organic singlecrystal optical microwaveguides. *Angew. Chem., Int. Ed.* 2020, *59*, 13821–13830.
- (54) Mishra, M. K.; Mukherjee, A.; Ramamurty, U.; Desiraju, G. R. Crystal chemistry and photomechanical behavior of 3,4dimethoxycinnamic acid: correlation between maximum yield in the solid-state topochemical reaction and cooperative molecular motion. *IUCrJ* 2015, *2*, 653–660.
- (55) Sahoo, S. C.; Nath, N. K.; Zhang, L.; Semreen, M. H.; Al-Tel, T. H.; Naumov, P. Actuation based on thermo/photosalient effect: a biogenic smart hybrid driven by light and heat. *RSC Adv.* 2014, *4*, 7640–7647.

57 58 59

Table of Content Graph

