Designing Site Specificity in the Mechanochemical Cargo Release of Small Molecules

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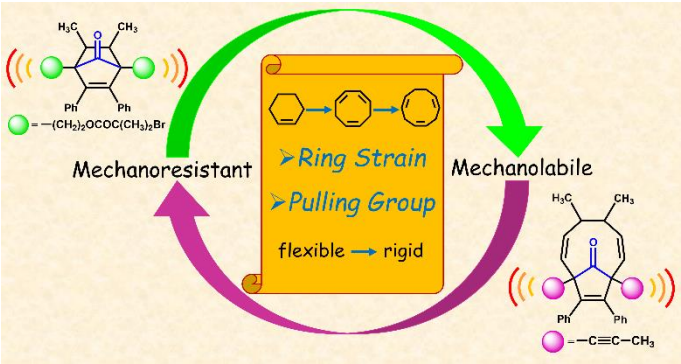
ABSTRACT

Mechanical force can trigger the predictable and precise release of small molecules from macromolecular carriers. It has been shown based on mechanochemical simulations, that norborn-2-en-7-one (NEO), I, and its derivatives can selectively release CO, N_2, and SO_2 and produce two distinctly different products, A ((3E,5Z,7E)-dimethyl-5,6-diphenyldeca-3,5,7-triene1,10-diyl bis(2-bromo-2-methylpropanoate)) and B (4′,5′-dimethyl-4′,5′-dihydro-[1,1′:2′,1′′-terphenyl]-3′,6′-diyl)bis(ethane-2,1-diyl) bis(2-bromo-2-methylpropanoate). Site-specific design ensures that by changing the regioselectivity, either A or B can be exclusively generated. Altering the NEO scaffold's rigidity is accomplished by replacing a 6-membered ring with an 8-membered ring and concomitantly fine-tuning the pulling groups, enabling mechanolability and the preferred formation of B. The diradical intermediate formed during I → A is predicted to be persistent for ∼150 fs. The structural design holds the key to the trade-off between mechanochemical rigidity and lability.



References

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