



Unveiling [3 + 2] cycloaddition reactions of benzonitrile oxide and diphenyl diazomethane to cyclopentene and norbornene: a molecular electron density theory perspective

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Abstract

A molecular electron density theory (MEDT) study is performed for the [3 + 2] cycloaddition (32CA) reactions of benzonitrile oxide (BNO) and diphenyldiazomethane (DPDM) to cyclopentene (CP) and norbornene (NBN) with the objective to analyse the experimentally observed acceleration in NBN reactions relative to the CP ones. The activation enthalpy of the 32CA reaction of NBN with BNO is lowered than that of CP by 2.1–2.9 kcal mol⁻¹ in gas phase, DMSO, acetonitrile and THF, while the corresponding differences are 1.3–1.8 kcal mol⁻¹ with DPDM. The 32CA reactions of DPDM show lower activation parameters compared to that of BNO consistent with the respective *pseudo(mono)radical* and zwitterionic type characters of DPDM and BNO. The *syn* diastereofacial approach of NBN is energetically feasible compared to the *anti* one. The global electron density transfer (GEDT) is identified to anticipate the minimal electron density flux at the TS entity, which is otherwise not accounted by the global electrophilicities of the separated reagents. This MEDT study allows comprehending that for these non-polar reactions, the acceleration in NBN cycloadditions compared to the CP ones is due to the relatively lower energy cost demanded for the depopulation and subsequent rupture of C–C double bond of NBN followed by sequential bonding changes along the reaction paths, rather than the “predistorted geometry towards the TSs” as previously proposed in the 32CA reactions of norbornene derivatives.

Keywords Molecular electron density theory · Norbornene · Benzonitrile oxide · Conceptual DFT · Electron localisation function

1 Introduction

Norbornene (NBN) (bicyclo [2.2.1] hept-2-ene) and its derivatives have established their promising practical applications in polymer science, solar energy converters, medicinal and agricultural chemistry over more than 60 years [1]. Very recently, the copolymerisation of NBN and divinyl benzene has been reported for the synthesis of graft polymers [2], while NBN derivatives have also found several current

applications in bioorthogonal reactions [3, 4]. The unique angularly strained structural geometry of NBN fosters its synthetic applicability as an attractive candidate in organic synthesis [1, 5–10]. The behaviour of NBN derivatives in ring opening metathesis polymerisation [5, 6], cycloaddition reactions [7], Wagner–Meerwein rearrangement [8], Prins reaction [9] and photochemical excitation [10] are well documented for synthetic applications.

In 2015, Truong et al. [7] reported the first application of the [3 + 2] cycloaddition (32CA) reaction of nitrile oxide **1** with NBN **2** to prepare hydrogels (Scheme 1). In 2016, Zhang et al. [11] performed the polyaddition of azide-containing NBN-based monomer for polymer resin industries. Several other applications [1] have placed the 32CA reactions of NBN derivatives in the top-shelf priority of applied chemistry and consequently invited chemists to explore the possibilities, design new strategies and analyse these reactions.

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