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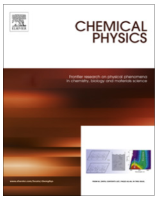

Assessment of theoretical procedures for a diverse set of isomerization reactions involving double-bond migration in conjugated dienes

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ABSTRACT

We introduce a representative database of 60 accurate diene isomerization energies obtained by means of the high-level, ab initio W*n*–F12 thermochemical protocols. The isomerization reactions involve a migration of one double bond that breaks the π-conjugated system. The considered dienes involve a range of hydrocarbon functional groups, including linear, branched, and cyclic moieties. This set of benchmark isomerization energies allows an assessment of the performance of more approximate theoretical procedures for the calculation of π-conjugation stabilization energies in dienes. We evaluate the performance of a large number of density functional theory (DFT) and double-hybrid DFT (DHDFT) procedures. We find that, with few exceptions (most notably BMK-D3 and M05-2X), conventional DFT procedures have difficulty describing reactions of the type: conjugated diene → non-conjugated diene, with root mean square deviations (RMSDs) between 4.5 and 11.7 kJ mol^{-1}. However, DHDFT procedures show excellent performance with RMSDs well below the 'chemical accuracy' threshold.

1. Introduction

Over the past two decades density functional theory (DFT) has become one of the most widely used electronic structure methods in materials and quantum chemistry due to its attractive accuracy-to-computational cost ratio relative to other electronic structure methods. With this increase in popularity there has been a proliferation in the number of developed DFT procedures [1]. The approximations for the XC functional can be classified according to their rung on Perdew's 'Jacob's Ladder of DFT': (1) the local density approximation (LDA); (2) pure generalized gradient approximation (GGA) employing both the local density and the reduced density gradient; (3) the meta-GGAs (mGGA) which additionally employ the kinetic energy density; (4) the hybrid-meta-GGAs (hmGGA) which additionally involve the occupied orbitals; and (5) the double-hybrid (DH) functionals which additionally employ the virtual orbitals [2,3]. While, in general, the accuracy of DFT increases as one climbs the rungs of Jacob's Ladder at present no truly systematic path towards the exact solution exists. Thus, the only validation for a given DFT approximation is benchmarking against accurate reference data. Ideally, the benchmark data should: (i) have well-defined error bars that are much smaller (preferably, by an order of magnitude or more) than the intrinsic error of the method being evaluated, and (ii) be as large and chemically diverse as reasonably possible [4–6].

It is well established that the performance of DFT (or for that matter of any approximate theoretical procedure) can vary for different types of reactions. In particular, the accuracy of a given approximate theoretical procedure should increase as larger molecular fragments are conserved on the two sides of the reaction, due to an increasing degree of error cancelation between reactants and products. For example, the performance of DFT improves along the sequence: atomization → isogyric → isodesmic → hypohomodesmotic → homodesmotic → hyperhomodesmotic reactions [7–13]. In the context of hydrocarbon isomerization reactions, it has been shown that the performance of DFT for linear alkane → branched alkane isomerizations is significantly better than that for isogyric structural isomerizations [8,14–20]. For example, the root mean square deviations (RMSDs) for a wide range of DFT methods for C_8H_8 isomer energy separations (which are mostly isogyric reactions in which the bonding situation is very different on both sides of the reaction) vary between 5.0 and 40 kJ mol^{-1} [15]. On the other hand, the RMSDs for a wide range of dispersion-corrected DFT for linear → branched alkane isomerizations (i.e., reactions that conserve the number of C atoms in each hybridization state in addition to being isodesmic) are about one order of magnitude smaller, i.e., they vary between 0.5 and 4.0 kJ mol^{-1} [10].

In the present work, we introduce a representative benchmark database of 60 diene isomerization energies (to be known as the

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DIE60 set). The reactions in the DIE60 database (Fig. 1) are of the type conjugated diene → non-conjugated diene. The database covers a broad spectrum of structures, including linear and branched dienes (C_nH_{2n-2}) and cyclic dienes (C_nH_{2n-4}) ($n = 5$, 6, and 7). Reference isomerization energies at the CCSD(T)/CBS level (i.e., complete basis set limit CCSD(T) energies) are obtained by means of the high-level W2–F12 procedure (for the C_5H_6, C_5H_8, C_6H_8, C_6H_{10}, and C_7H_{10} dienes) or with the W1–F12 procedure (for the C_7H_{12} dienes) [21]. These benchmark values allow us to assess the performance of more approximate theoretical procedures for

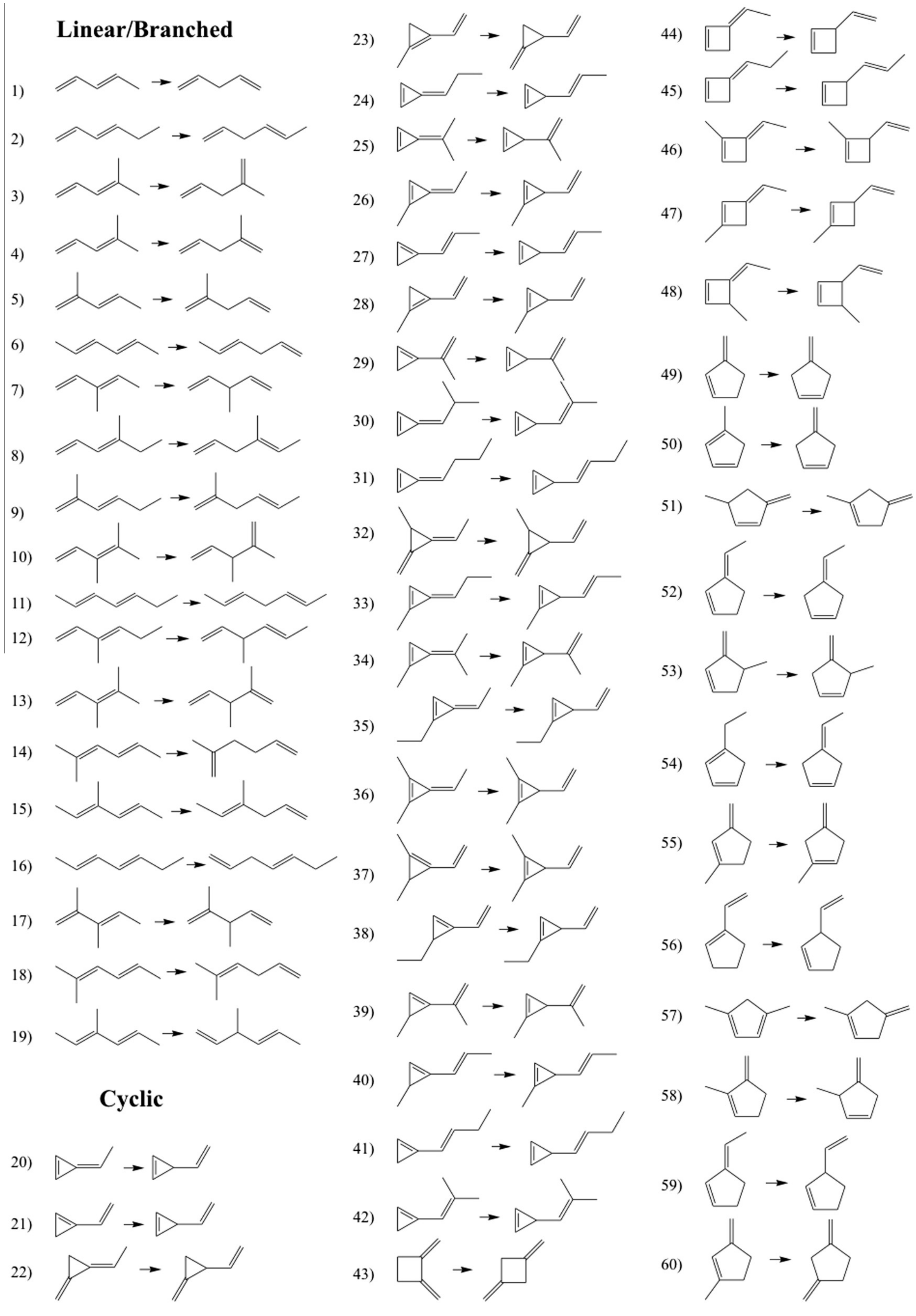

Fig. 1. Isomerization reactions in the DIE60 database.