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Synthesis, Stereochemistry, and Photochemical and Thermal Behaviour of bis-t-Butyl Substituted Overcrowded Alkenes

Supplementary Information

Matthijs K. J. ter Wiel, Marcin G. Kwit, Auke Meetsma, Ben L. Feringa*
Department of Organic and Molecular Inorganic Chemistry, Stratingh Institute, University of Groningen, Nijenborgh 4, 9747 AG Groningen, The Netherlands, Tel: +31 50 363 4278, Fax + 31 50 363 4296, E-mail: Feringa@chem.rug.nl

Calculations

At first the relation between the energy of molecule and its structure was estimated at the AM1 semi-empirical level. The dihedral angle C_2-C_1-$C_{1'}$-$C_{2'}$ was rotated anticlockwise with steps of 10º, and for each structure the heat of formation was calculated. This allowed construction of a potential energy surface (PES) and selection of four stable conformers representing energy minima. These structures were further optimised at the b3lyp/6-31g(d)//b3lyp/3-21g(d) level. For each structure frequencies were calculated at the b3lyp/3-21g(d) level, confirming that those structures are stable. Selected calculated structural parameters of all four isomers of **4** are collected in table 1. It should be noted, however, that the energy maxima found on the PES do not reflect the barriers of activation for the thermal helix inversions.

Table S1 Calculated structures for the four isomers of **4** and the experimental structural data of stable *cis*-**4** and stable *trans*-**4**.

	stable *cis*-**4**		unstable *cis*-**4**	stable *trans*-**4**		unstable *trans*-**4**
	DFT	X-ray	DFT	DFT	X-ray	DFT
ΔE (kJ·mol^{-1})	0.0		+26.5	+11.0		+20.2
C_1-C_1	1.354 Å	1.365 Å	1.364 Å	1.354 Å	1.350 Å	1.363 Å
C_2-C_1-C_{9b}	104.8°	105.0°	105.9°	104.3°	104.2°	105.4°
C_2-C_1-$C_{1'}$	122.3°	121.6°	124.4°	125.6°	126.0°	126.6°
C_{9b}-C_1-$C_{1'}$	132.7°	133.2°	129.6°	126.6°	127.4°	127.2°
C_2-C_1-$C_{1'}$-$C_{2'}$	16.8°	11.0°	-30.7°	-153.3°	-162.2°	145.5°
C_{9b}-C_1-$C_{1'}$-$C_{9b'}$	-5.8°	-3.2°	-24.4°	158.2°	155.8°	165.4°
C_2-C_1-$C_{1'}$-$C_{9'b}$	-168.7°	-176.1°	152.5°	2.4°	-3.2°	-26.0°
C_1-$C_{1'}$-$C_{9'b}$-$C_{9'a}$	34.2°	31.5°	-27.1°	48.1°	44.4°	-36.6°
C_1-$C_{1'}$-$C_{2'}$-$C_{2'C}$	-93.6°	-96.4°	-34.1°	-120.9°	-116.2°	-22.0°

The comparison of calculated structures with experimental X-ray data shows excellent agreement and shows that this semi-empirical-DFT methodology can be used for the prediction of structurally related molecules.

The lowest-energy isomers of **4** were then used as starting points for the computation of accessible isomers of **5**. First, the methyl groups at C_2 and $C_{2'}$ in the stable forms of **4** were replaced by *t*-butyl substituents and full structure optimisations were performed for all compounds at the AM1 semi-empirical level, followed by systematic conformational search at the same level for each previously optimised structure according to the procedure described for **4**. Again, four energy minima were found that were fully optimised by the DFT method at the b3lyp/3-21g(d) level. For these structures frequency calculations were carried out at the same level of theory (b3lyp/3-21g(d)) to confirm the stability of the conformation. Additionally single point energies at the b3lyp/6-31g(d) level were calculated for each structure. Selected structural parameters are depicted in table 2.

Table S2 Calculated structures for all four isomers of **5** and the experimental data for both *cis*-isomers of **5** from X-ray crystallography.

	stable *cis*-**5**		unstable *cis*-**5**		stable *trans*-**5**	unstable *trans*-**5**
	DFT	X-ray	DFT	X-ray	DFT	DFT
ΔE (kJ·mol^{-1})	0.0		+57.5		+42.0	+89.7
C_1-C_1	1.356 Å	1.353 Å	1.380 Å	1.379 Å	1.359 Å	1.374 Å
C_2-C_1-C_{9b}	104.4°	104.1°	107.4°	107.0°	104.1°	104.6°
C_2-C_1-$C_{1'}$	124.9°	124.2°	121.1°	120.4°	145.1°	129.9°
C_{9b}-C_1-$C_{1'}$	129.5°	130.9°	131.5°	132.6°	123.8°	104.6°
C_2-C_1-$C_{1'}$-$C_{2'}$	-19.0°	-13.5°	-40.2°	-37.3°	145.1°	-136.8°
C_{9b}-C_1-$C_{1'}$-$C_{9b'}$	9.6°	10.9°	-43.5°	-39.6°	-142.4°	143.0°
C_2-C_1-$C_{1'}$-$C_{9'b}$	175.3°	178.7°	138.1°	141.6°	1.3°	-40.1°
C_1-$C_{1'}$-$C_{9'b}$-$C_{9'a}$	-44.9°	-44.8°	-72.0°	-73.7°	-62.6°	-36.1°
C_1-$C_{1'}$-$C_{2'}$-$C_{2'C}$	-105.9°	102.6°	-7.9°	-6.4°	-130.5°	-24.6°