

Unlocking n-alk-1-ynes Conformers: Quantum “Trigger Finger” versus “Stiff Joint” Conformations

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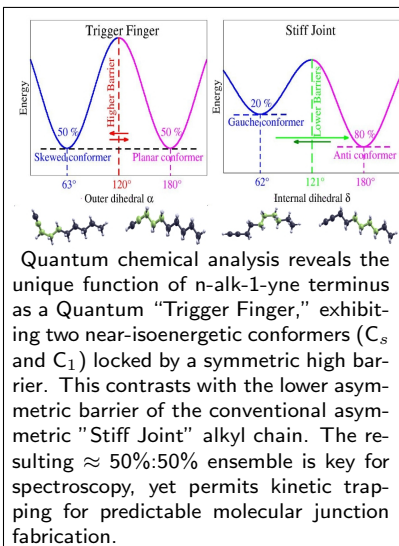
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Abstract

Molecular conformation in n-alk-1-yne (CnA) is conventionally simplified to an all-planar structure. We report a comprehensive quantum chemical analysis revealing two near-isoenergetic rotamers at the acetylenic terminus: planar (C_s) and skewed (C_1). The high, symmetric rotational energy barrier (≈ 150 meV) arises from unique steric relief near the sp center coupled with electronic stabilization of C_1 . This creates a unique kinetic profile: a Quantum “Trigger Finger” (α rotation) that enforces an $\approx 50\% : 50\%$ C_s/C_1 ensemble, sharply contrasting with the thermodynamically biased “Stiff Joint” (δ rotation) of the alkyl chain. This structural degeneracy necessitates ensemble averaging for spectroscopic data interpretation, while the slow interconversion permits kinetic trapping and intentional conformer enrichment during synthesis and molecular junction fabrication. Our work redefines the alkyne anchor, providing a blueprint for accurate interpretation of spectroscopic data and achieving conformational control in molecular electronics.

TOC Graphic



Keywords

Alkyne Conformation • Hyperconjugation • Quantum Chemistry • Kinetic Control • Molecular Electronics

While alkyne ($\text{C}\equiv\text{CH}$) terminals possess favorable properties (stability and strong electronic coupling) that suggest their broad use as robust anchors for molecular devices, this potential has not translated into widespread adoption. In the field of molecular junctions, thiols overwhelmingly dominate the literature,¹⁻¹³ and the use of n-alk-1-yne (CnA , $\text{HC}\equiv\text{C}-\text{CF}_2-(\text{CH}_2)_{n-1}-\text{CH}_3$) in fabricating such devices is exceedingly rare, with only three publications¹⁴⁻¹⁶ reporting CnA -based junctions to date. This minimal experimental adoption is coupled with a persistent theoretical blind spot: the prevailing convention assumes an all-planar alkyne conformation (C_s), a fact reinforced by the total absence of the non-planar C_1 conformer (to which the present study is mainly devoted) in the NIST database.¹⁷ This fundamental gap in both experimental data and foundational structural recognition—which our investigation was triggered by—necessitates a comprehensive quantum chemical re-evaluation of the conformational landscape of the alkyne anchor.

This work presents a comprehensive quantum chemical analysis that resolves this long-standing ambiguity, revealing that the acetylenic terminus acts as a unique conformational element with two stable rotamers (C_s and C_1). Our findings demonstrate that the C_1 conformer is an intrinsic, kinetically persistent component of the molecular conformer ensemble, a fact vital, e.g., for accurate interpretation of spectroscopic data and measurements on molecular electronic devices.

Conformational Profile: The Terminal α Dihedral

Our investigation confirms the existence of two stable, low-energy rotamers governed by the terminal α dihedral angle: the planar (C_s , $\alpha = 180^\circ$) and the non-planar skewed (C_1 , $\alpha \approx 63^\circ$) conformers (Figure 1, bond metric data in Table 1).

Multiple DFT and high-level composite thermochemistry methods consistently confirmed that C_s and C_1 are nearly isoenergetic, with $\Delta G < 0.2 \text{ kcal/mol}$ (Table 2). As illustrated in Figure 2a and b, the energetic ordering is highly sensitive to the functional employed, confirming the subtle and near-degenerate nature of the terminal conformational landscape.

Table 1: Bond metrics versus size for planar and skewed CnA = H-C $\equiv$ C-(CH₂)_{n-1}-CH₃ conformers optimized using the M06-2X exchange-correlation functional with GD3 dispersion corrections and CC-pVTZ basis sets.¹⁸

CnA	Conformer	max r(H,H)	r(C1,Cn)	r(C1,C2)	r(C2,C3)	r(C3,C4)	$\angle$ C ₂ C ₃ C ₄ C ₅	$\angle$ C ₂ C ₃ C ₄	$\angle$ C ₃ C ₄ C ₅
C2A	planar	5.5488	3.5208	1.1975	1.4609	1.5302	N/A	112.208	N/A
	skewed	5.5487	3.5206	1.1975	1.4609	1.5302	N/A	112.197	N/A
C3A	planar	6.6685	4.9566	1.1975	1.4599	1.5320	179.999	112.670	111.548
	skewed	5.5460	3.8170	1.1977	1.4613	1.5341	62.712	112.571	112.552
C4A	planar	7.9901	6.0336	1.1975	1.4599	1.5313	180.000	112.647	112.152
	skewed	6.7599	5.1565	1.1977	1.4613	1.5332	63.344	112.642	113.133
C5A	planar	9.1685	7.4223	1.1975	1.4599	1.5315	179.997	112.643	112.121
	skewed	7.5016	5.9347	1.1977	1.4613	1.5334	63.369	112.623	113.105
C6A	planar	10.4827	8.5677	1.1975	1.4599	1.5314	180.000	112.647	112.116
	skewed	8.5622	7.3203	1.1977	1.4614	1.5333	63.355	112.622	113.084
C7A	planar	11.6875	9.9286	1.1975	1.4598	1.5314	179.993	112.649	112.114
	skewed	9.7357	8.2885	1.1977	1.4613	1.5333	63.369	112.619	113.083
C8A	planar	12.9954	11.1065	1.1975	1.4599	1.5314	179.997	112.651	112.113
	skewed	10.8224	9.6720	1.1977	1.4613	1.5333	63.255	112.629	113.084
C9A	planar	14.2145	12.4497	1.1975	1.4599	1.5314	179.994	112.654	112.113
	skewed	12.0938	10.7295	1.1977	1.4613	1.5333	63.323	112.624	113.090
C10A	planar	15.5185	13.6474	1.1975	1.4599	1.5314	179.999	112.654	112.110
	skewed	13.2306	12.1002	1.1977	1.4614	1.5333	63.382	112.618	113.085
C11A	planar	16.7474	14.9789	1.1975	1.4599	1.5314	179.994	112.657	112.110
	skewed	14.5186	13.2105	1.1978	1.4613	1.5333	63.101	112.645	113.098
C12A	planar	18.0478	16.1896	1.1975	1.4599	1.5314	179.996	112.656	112.110
	skewed	15.7648	14.5735	1.1977	1.4614	1.5333	63.133	112.640	113.097
C13A	planar	19.2832	17.5125	1.1975	1.4599	1.5314	179.997	112.657	112.109
	skewed	17.0318	15.7096	1.1978	1.4614	1.5333	63.217	112.635	113.094
C14A	planar	20.5803	18.7320	1.1975	1.4599	1.5314	179.999	112.655	112.109
	skewed	18.3081	17.0618	1.1977	1.4614	1.5333	63.244	112.629	113.095
C15A	planar	21.8211	20.0488	1.1975	1.4598	1.5315	179.991	112.660	112.107
	skewed	19.5758	18.2186	1.1977	1.4614	1.5333	63.381	112.615	113.089

The two states are separated by a symmetric rotational energy barrier of approximately 150 meV (Figure 2). This barrier is consistent across chain lengths (n) and establishes the kinetic persistence of the individual conformers at room temperature. Furthermore, analysis using the polarizable continuum model (GAUSSIAN keyword IEFPCM¹⁸) confirmed that the barrier height and energetic degeneracy are robustly maintained in a range of representative solvents: non-polar (cyclohexane, toluene), weakly polar (dichloromethane), and polar (acetonitrile) (Figure 2c). This validated that the rotational profile is an intrinsic molecular property driven by internal electronic and steric factors.

Structural and Electronic Origin of Non-Planarity

The existence and near-degeneracy of the non-planar C₁ state is dictated by a unique interplay of steric relief and electronic stabilization at the acetylenic terminus.

Table 2: Conformer stability difference ($\Delta G = G_{\text{skewed}} - G_{\text{planar}}$) based on Gibbs Free Energy in kcal/mol (298 K) for *n*-alk-1-yne molecules (CnA) spanning C2A to C15A. A positive sign indicates the planar conformer is more stable, while a negative sign indicates the skewed conformer is more stable, as confirmed by the indicator in parentheses.

CnA	G3	G4	CBS-QB3	CBS-4M
C2A	-0.002 (skewed)	0.000 (equal)	+0.001 (planar)	-0.006 (skewed)
C3A	-0.044 (skewed)	+0.034 (planar)	-0.009 (skewed)	-0.028 (skewed)
C4A	-0.061 (skewed)	+0.044 (planar)	-0.011 (skewed)	-0.068 (skewed)
C5A	-0.090 (skewed)	+0.029 (planar)	-0.011 (skewed)	-0.116 (skewed)
C6A	-0.100 (skewed)	+0.015 (planar)	-0.024 (skewed)	-0.149 (skewed)
C7A	-0.122 (skewed)	-0.005 (skewed)	-0.017 (skewed)	-0.142 (skewed)
C8A	-0.073 (skewed)	-0.033 (skewed)	-0.068 (skewed)	-0.158 (skewed)
C9A	-0.090 (skewed)	-0.028 (skewed)	-0.035 (skewed)	-0.142 (skewed)
C10A	-0.118 (skewed)	-0.048 (skewed)	-0.083 (skewed)	-0.164 (skewed)
C11A	-0.100 (skewed)	+0.057 (planar)	+0.034 (planar)	-0.154 (skewed)
C12A	-0.081 (skewed)	+0.063 (planar)	-0.018 (skewed)	-0.161 (skewed)
C13A	-0.109 (skewed)	0.000 (equal)	0.000 (equal)	-0.157 (skewed)
C14A	-0.142 (skewed)	0.000 (equal)	-0.027 (skewed)	-0.183 (skewed)
C15A	-0.144 (skewed)	+0.061 (planar)	-0.043 (skewed)	-0.159 (skewed)

Steric Relief at the α -Carbon

The core structural difference lies in the nature of the rotating bonds. While the internal δ -rotation involves an $\text{sp}^3 - \text{sp}^3$ $\text{CH}_2 - \text{CH}_2$ bond, where the steric penalty (≈ 20 meV) arises from the clash between the four hydrogen atoms on the two δ carbons, the terminal α -rotation is fundamentally an $\text{sp} - \text{sp}^3$ rotation ($\text{C}2 - \text{C}3$). The steric environment is entirely different because the sp -hybridized carbon ($\text{C}2$) is not bonded to any hydrogen atoms that could participate in a local gauche clash. This dramatic structural change provides significant steric relief, effectively suppressing the traditional gauche penalty. With the steric cost eliminated, the stability of the non-planar C_1 state is governed by favorable electronic effects, specifically $\pi_{\text{C}\equiv\text{C}} \rightarrow \sigma_{\text{C}-\text{H}}^*$ hyperconjugation, allowing it to achieve energy comparable to the planar C_s state.

Validation via Fluorination

To further probe the mechanistic origin of the C_s/C_1 near-degeneracy, the fluorinated analog, 2,2-difluoro-n-oct-1-yne (F2-C8A, $H-C \equiv C-CF_2-(CH_2)_6-CH_3$), was studied (Table 3). Evaluation using the most reliable composite methods (G3, G4, CBS-QB3) confirms that

Table 3: Comparison of conformational metrics for 1-decyne (C8A = $H-C \equiv C-(CH_2)_7-CH_3$) and fluorinated decyne (F2-C8A = $H-C \equiv C-CF_2-(CH_2)_6-CH_3$) computed at the M06-2X/GD3 level of theory.¹⁸ X_3 is the H or F atom closest to the center (M) of the triple bond $C_1 \equiv C_2$.

Mol.	Conformer	r(C1,C2)	r(C2,C3)	r(C3,C4)	r(C1,C10)	d(X3,M)	$\angle X_3MC_2$	α
C8A	planar	1.1975	1.4599	1.5314	11.1065	2.6302	22.514	179.997
F2-C8A	planar	1.1942	1.4714	1.5134	11.0756	2.8271	26.169	179.999
C8A	skewed	1.1977	1.4613	1.5333	9.6720	2.6239	22.884	63.256
F2-C8A	skewed	1.1943	1.4722	1.5120	9.7052	2.8242	26.489	60.855

the near-degeneracy persists in F2-C8A ($|\Delta G| < 0.4$ kcal/mol), but the energetic ordering becomes slightly more pronouncedly skewed (C_1 favored) compared to C8A (Table 4). This

Table 4: Conformational stabilities for 1-decyne (C8A = $H-C \equiv C-(CH_2)_7-CH_3$) and fluorinated decyne (F2-C8A = $H-C \equiv C-CF_2-(CH_2)_6-CH_3$) using different compound chemistry models.¹⁸ Differences in Gibbs free energy ($\Delta G = G_{\text{torsioned}} - G_{\text{planar}}$) are given in kcal/mol. The negative values indicate the torsioned (skewed) rotamer is more stable.

Method	ΔG C8A	ΔG F2-C8A
G3	-0.073	-0.344
G4	-0.033	-0.178
CBS-QB3	-0.068	-0.315
CBS-4M	-0.158	-0.113

confirms the equilibrium is exquisitely sensitive to the electronic environment, as expected for a $\Delta G \approx 0$ system. The substitution provides three key structural and electronic validations:

- Steric Test Passed: Despite the larger size of the fluorine atom, the near-zero ΔG is maintained, confirming the sp hybridization fundamentally nullifies the steric cost of the non-planar conformation.

- **Electronic Sensitivity Confirmed:** The C2–C3 single bond lengthens upon fluorination (e.g., 1.4613 Å in C8A to 1.4722 Å in F2 – C8A, cf. Table 3). This lengthening indicates the powerful inductive effect of the CF₂ group strongly influences the σ -framework.
- **Compensatory Electronic Balance:** While the hyperconjugative stabilization of C₁ is weakened by the C–F substitution (distance d(F3, M) larger than d(H3, M), cf. Table 3), the overall ΔG remains near zero. This outcome reveals a critical electronic balance: the loss of C – H... π stabilization is effectively compensated by the strong inductive withdrawal of the CF₂ group. The C_s/C₁ balance is thus confirmed to be the result of competing electronic forces that are highly tunable by substitution.

Kinetic Contrast: Quantum “Trigger Finger” vs. “Stiff Joint”

The CnA system’s kinetic profile is defined by the stark contrast between the terminal α rotation and the internal sp³ – sp³ δ rotation. The comparison is best described by the analogy of a binary, kinetically locked switch versus a conventionally biased joint.

The α Dihedral: The Kinetic Toggle Switch (“Trigger Finger”)

The behavior of the α dihedral (C $\equiv$ C – C – C) in n-alk-1-ynes can be described as a “Trigger Finger” (*tenosynovitis stenosans*): a medical condition where a tendon catches on its protective sheath, causing the finger to lock abruptly in a bent position. This mechanism captures the essential kinetic nature of the α -dihedral locking a binary state. The switch’s function is defined by:

- **The States (Near-Degeneracy):** The minimal energy difference ($|\Delta E| \leq 0.2$ kcal/mol) makes the planar (C_s) and staggered (C₁) states practically isoenergetic. This binary energy profile is the essence of the switch.
- **The Detent (≈ 150 meV Barrier):** The high ≈ 150 meV rotational barrier acts as the molecular kinetic lock (the “detent”). Since this energy significantly exceeds thermal

energy (~ 25 meV at room temperature), interconversion is suppressed, enforcing an abrupt, switch-like behavior rather than continuous rotation.

The resulting nearly symmetric rotational energy barrier defines the chemical and kinetic behavior of the alkyne terminus, leading to the key feature of an $\approx 50\% : 50\%$ ($C_s : C_1$) equilibrium mixture in gas or solution.

The δ Dihedral: The Stiff Joint

In contrast, the internal $sp^3 - sp^3$ δ dihedral is analogous to a Stiff Joint in the human body (like a knee or elbow) that has a clear, built-in energetic preference for the extended position:

- **The Preferred State (Built-in Energy Penalty):** The anti ($\delta = 180^\circ$) state is the global minimum. The gauche ($\delta \approx 62^\circ$) state is intrinsically less stable by ≈ 20 meV due to the steric clash between the four CH_2 hydrogen atoms.
- **The Asymmetric Resistance:** The resulting rotational barrier is asymmetric (≈ 110 meV for gauche $\rightarrow$ anti vs. ≈ 130 meV for anti $\rightarrow$ gauche). This energy difference reflects the inherent, thermodynamic preference for the anti state, confirming it is a conventional alkyl chain rotamer that is always biased toward linearity, resulting in a typical $\approx 80\%$ (anti) versus $\approx 20\%$ (gauche) distribution at room temperature.

Implications: Ensemble Analysis and Conformational Control

The persistent C_s/C_1 co-existence is an intrinsic, kinetically accessible feature of the acetylenic anchor that mandates a dual approach for its application.

- **Spectroscopic Necessity and Ensemble Average:** The stable equilibrium mixture is $\approx 50\% : 50\%$. Consequently, any measurement reflecting the state of the ensemble (e.g., standard gas- and solution-state spectroscopic data) must be interpreted as the ensemble average of these two distinct conformers. This necessitates that data analysis explicitly attempt to separate and identify the contributions from both C_s and C_1 .

- Kinetic Enrichment and Molecular Junctions: The slow $C_s \rightleftharpoons C_1$ interconversion rate permits significant kinetic trapping. By utilizing an appropriate synthesis pathway and preserving the product at low temperatures, one can relatively facily enrich the mixture, leading to an intentional imbalance in the C_s/C_1 ratio. This enriched conformational imbalance can be preserved when the molecule is integrated into a device, such as in the fabrication of molecular junctions or self-assembled monolayers, allowing for targeted studies where the impact of a non-50% : 50% distribution (the setting of the “Trigger Finger”) can be analyzed.

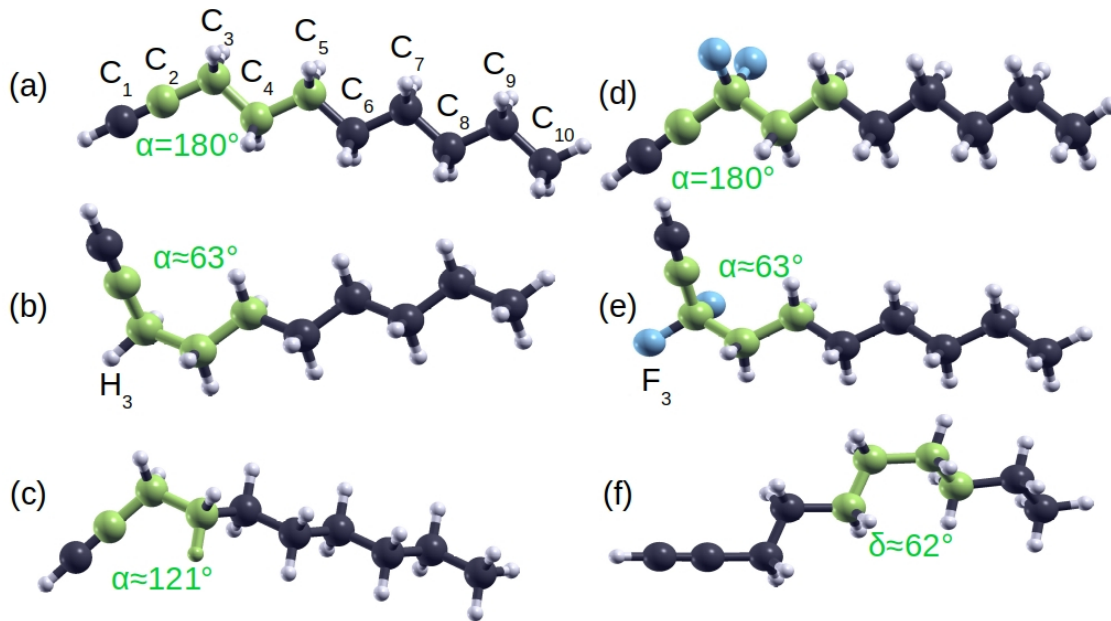


Figure 1: Optimized geometries for 1-decyne (C8A) and fluorinated decyne (F2 – C8A). The C atoms defining the α - and δ -dihedral angles are highlighted in green. (a, b) Planar (C_s) and skewed (C_1) α -conformers of C8A. (c) Eclipsed transition state ($\alpha \approx 120^\circ$). (d, e) Planar (C_s) and skewed (C_1) α -conformers of F2 – C8A. (f) Nonplanar conformer with internal gauche motif ($\delta \approx 62^\circ$). IUPAC numbering is shown in panel (a).

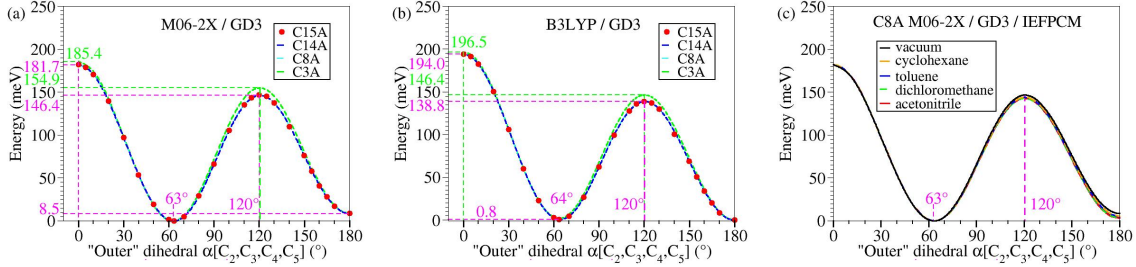


Figure 2: Conformational energy profile for the terminal α dihedral angle ($\angle[C_2, C_3, C_4, C_5]$). Profiles shown are in vacuo for various chain lengths n (a) M06-2X and (b) B3LYP, and (c) M06-2X/IEFPCM for C8A in representative solvents. The consistent, nearly symmetric and ≈ 150 meV barrier separates the near-isoenergetic planar (C_s) and skewed (C_1) minima. Solvent effects are negligible.

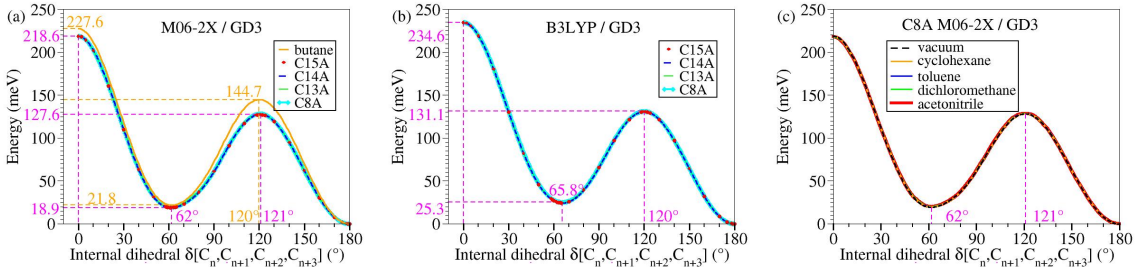


Figure 3: Conformational energy profile for the internal δ dihedral angle ($\angle[C_k, C_{k+1}, C_{k+2}, C_{k+3}]$) along the alkyl backbone. Profiles shown are in vacuo for various chain lengths n (a) M06-2X and (b) B3LYP, and (c) M06-2X/IEFPCM for C8A in solvents. The profile shows a thermodynamic preference for the anti (planar) state (≈ 20 meV) and an asymmetric barrier (≈ 110 meV vs. ≈ 130 meV), significantly lower than the symmetric α -barrier (Figure 2).

The insights gained in this work into the origin and stabilization of the nonplanar alkyne terminus are essential for interpreting spectroscopic data, rationalizing the reactivity of alkynes, and contributing to their improved functionality as anchoring groups in molecular electronic devices. We establish the terminal C₂–C₃ bond as a discretely switchable, kinetically locked element, elevating the n-alk-1-yne anchor to a sophisticated structural motif.

I gratefully acknowledge computational support by the state of Baden-Württemberg through bwHPC and the German Research Foundation through Grant Nos. INST 40/575-1, 35/1597-1, and 35/1134-1 (JUSTUS 2, bwUniCluster 2/3, and bwForCluster/MLS&WISO/HELIX 2).

Conflict of Interest

No conflict of interest to declare.

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