

Насколько длинной может быть C—C связь?

Синергия экспериментальных и теоретических исследований

Вишневский Юрий Викторович

2023

Вместо предисловия

THEO
CHEM

Journal of Molecular Structure (Theochem) 592 (2002) 1–6

Experiments, calculation, computation: in a shifting balance[☆]

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Вместо предисловия

Structural Chemistry (2023) 34:1225–1230
<https://doi.org/10.1007/s11224-023-02167-3>

EDITORIAL

Requiem for gas-phase electron diffraction

István Hargittai¹ · Magdolna Hargittai¹

“With further improvement of the computational possibilities, the diffraction data were playing a diminishing role in the combined analysis. It was increasingly realized that for many tasks, computation alone sufficed.”

Мой комментарий:

Это не означает, что ГЭ больше не нужна! Наоборот, имеется огромная потребность в точных экспериментальных структурах, т.к. доступные КХ приближения показывают сомнительную надежность на сложных объектах.

Типичная калибровка теории

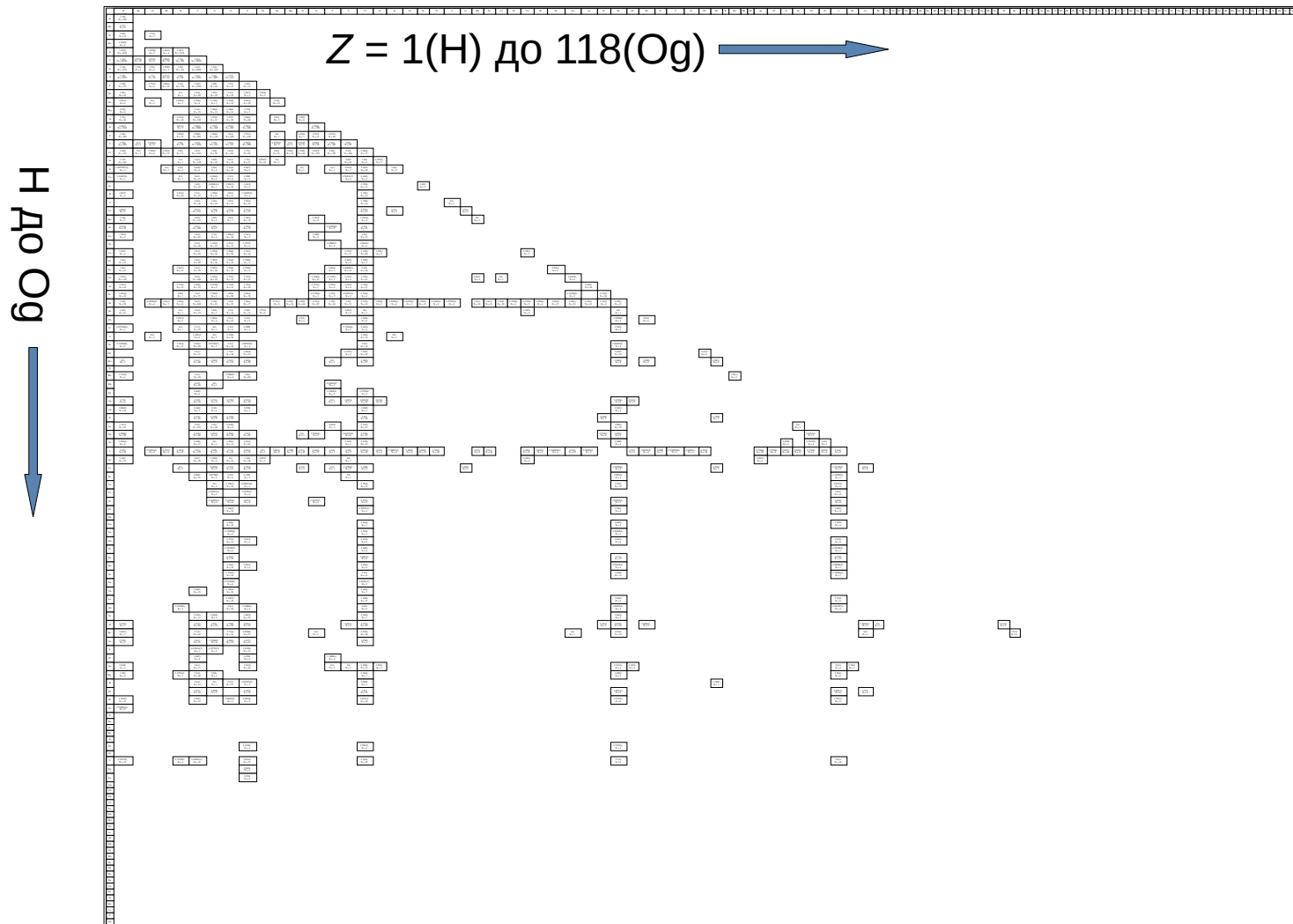
Molecule	Bond	Calculated	Experiment
ClOH	R_{OH}	96.3125	96.35(25)
HCP	R_{CH}	107.0748	107.02(10)
H ₂ CS	R_{CH}	108.5374	108.56(21)
CINO	R_{NO}	113.5837	113.357(25)
OCS	R_{CO}	115.6183	115.617(14)
HBS	R_{HB}	116.9857	116.98(4)
HCl	R_{HCl}	127.3669	127.455
FBS	R_{FB}	127.7466	127.62(2)
H ₂ S	R_{HS}	133.5272	133.56
PH ₃	R_{PH}	141.1539	141.16(6)
SO ₃	R_{SO}	141.7940	141.75(20)
SO ₂	R_{SO}	143.1144	143.080(1)
S ₂ O	R_{SO}	145.5467	145.7(15)
SiH ₄	R_{SiH}	147.4221	147.418
PN	R_{PN}	149.1431	149.0866
SiO	R_{SiO}	151.1653	150.9739
HSiCl	R_{SiH}	151.469	151.40
SiH ₂	R_{SiH}	151.2962	151.40

Проблемы:

- только маленькие молекулы.
- нет тяжелых атомов.
- нет комбинаций “сложных” атомов,
- игнорирование прецизионности параметров.

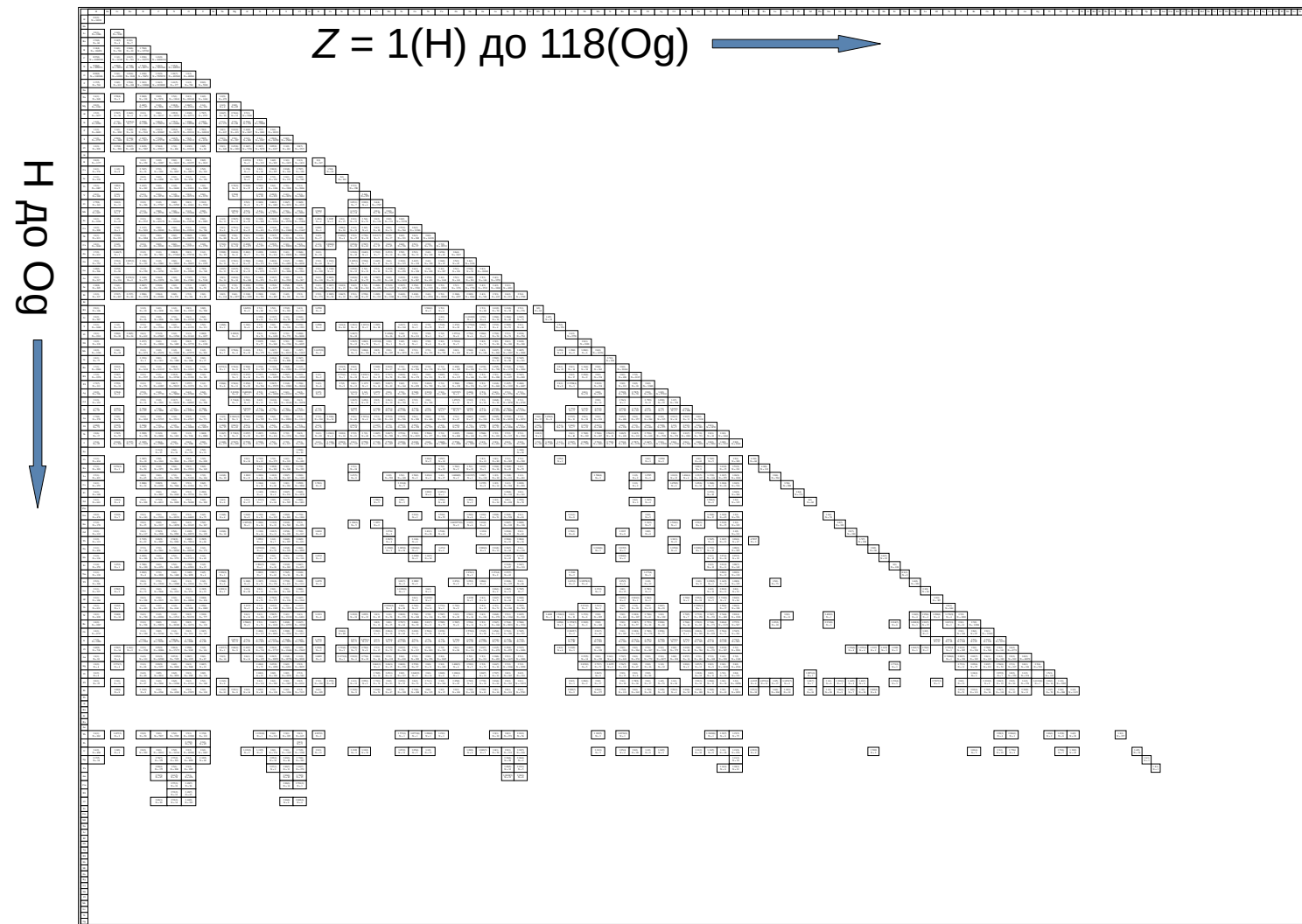
S. Coriani, D. Marchesan, J. Gauss, C. Hättig, T. Helgaker, P. Jørgensen, *J. Chem. Phys.* 2005, 123, 184107.

Газовая фаза: связи в MOGADOC (10.3K структур)



Проблема:
большинство
комбинаций не
исследовано!

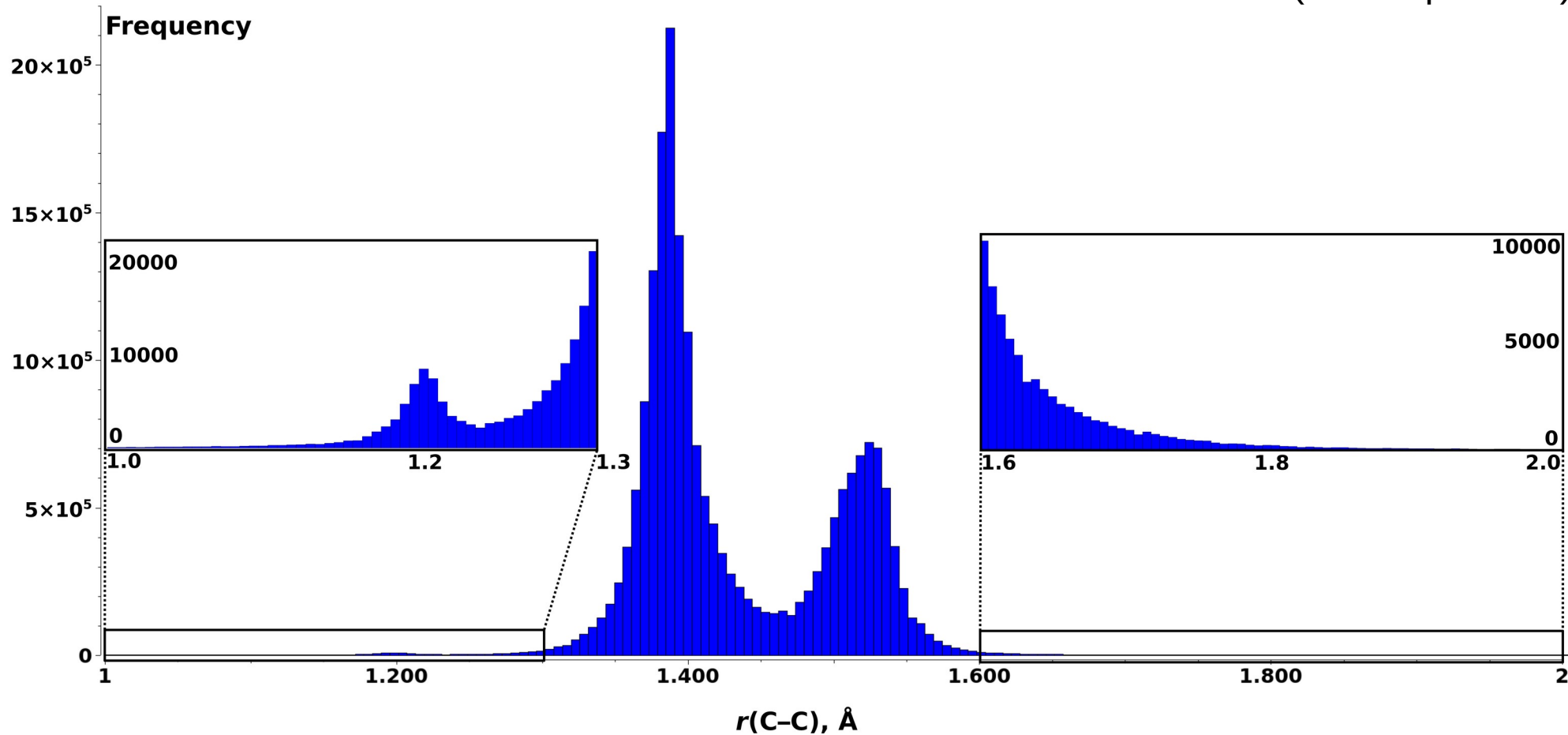
Твёрдая фаза: связи в CSD (1.2М структур)



Проблема:
молекулы в
кристаллах (сильно)
деформированы!

$r(\text{C}-\text{C})$ в кристаллах

CSD 5.43 (сентябрь 2022)

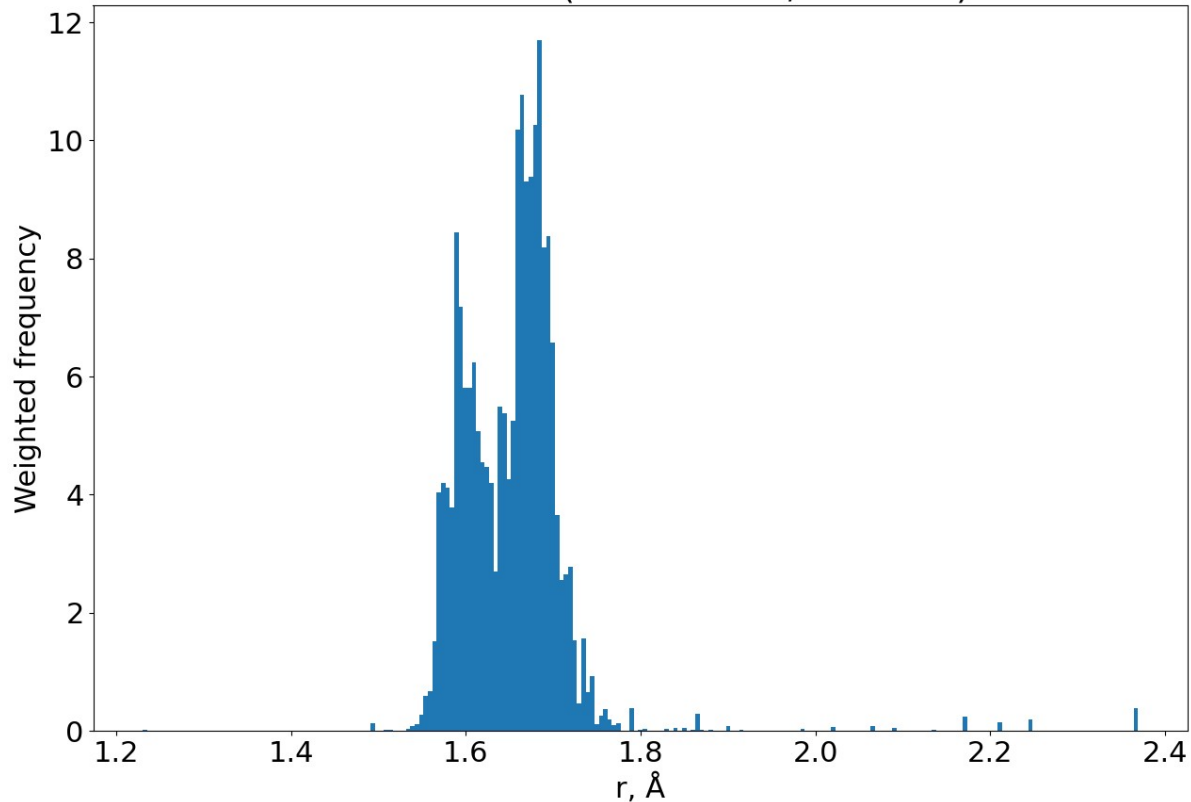


Осторожно, статистика в кристаллах!

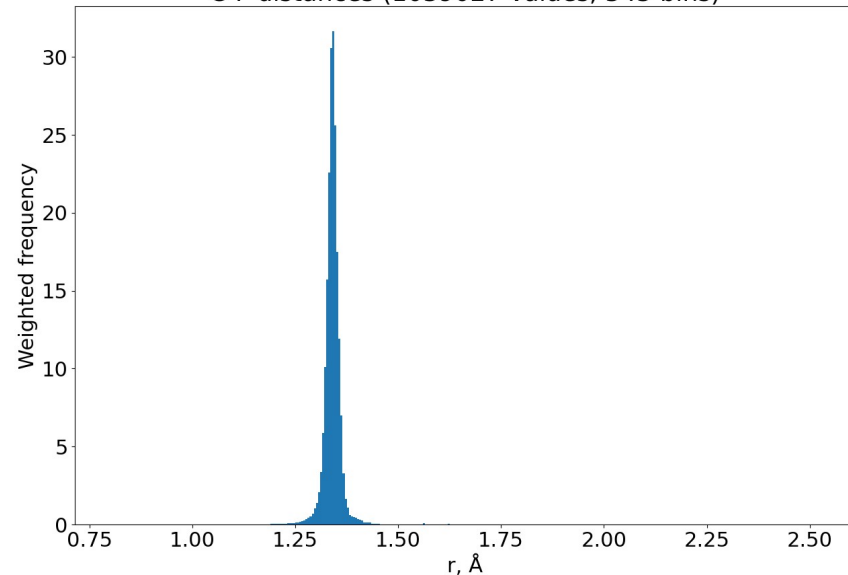
CSD: распределение $r(\text{Si-F})$:

Для сравнения, $r(\text{C-F})$:

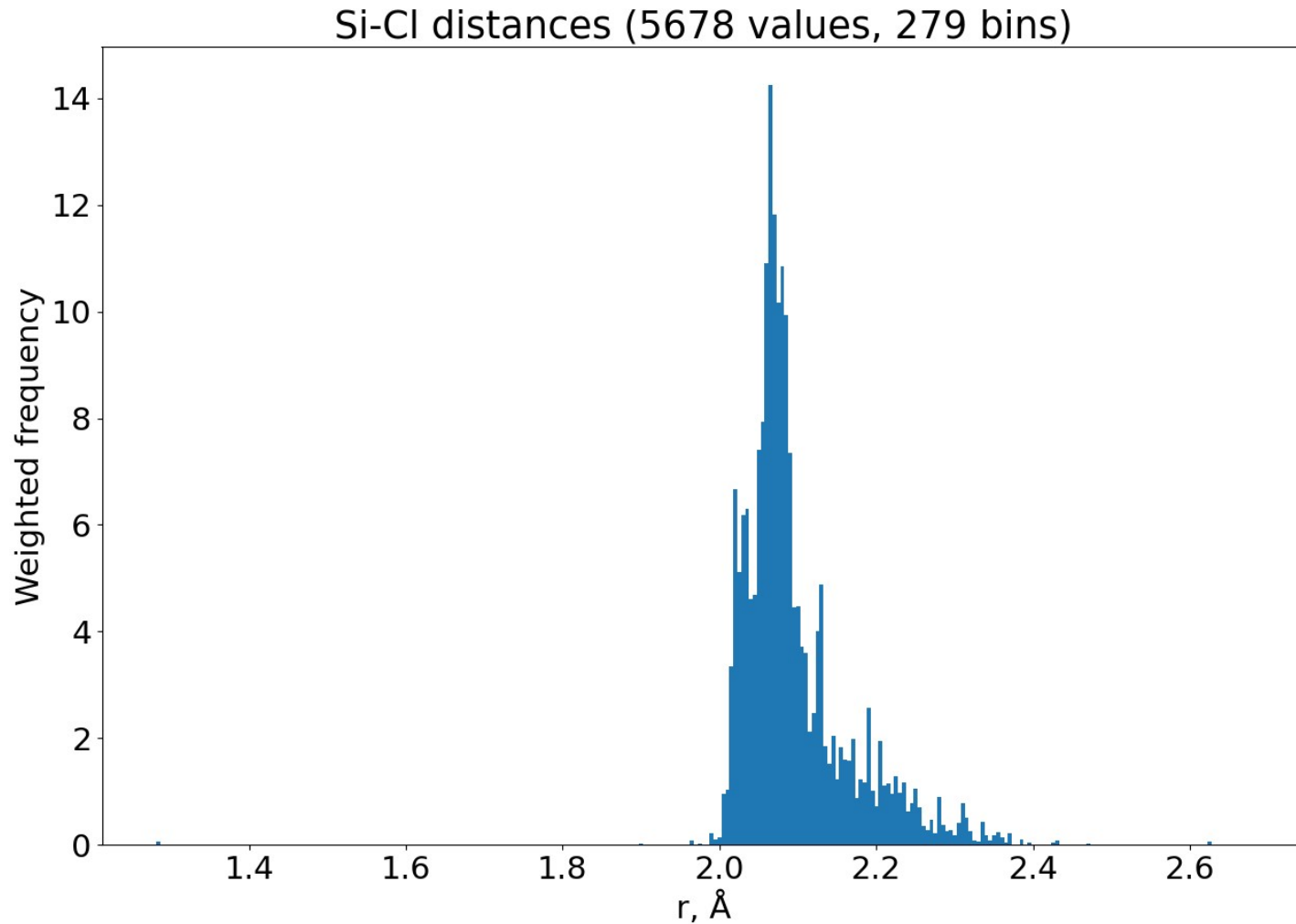
F-Si distances (7084 values, 227 bins)



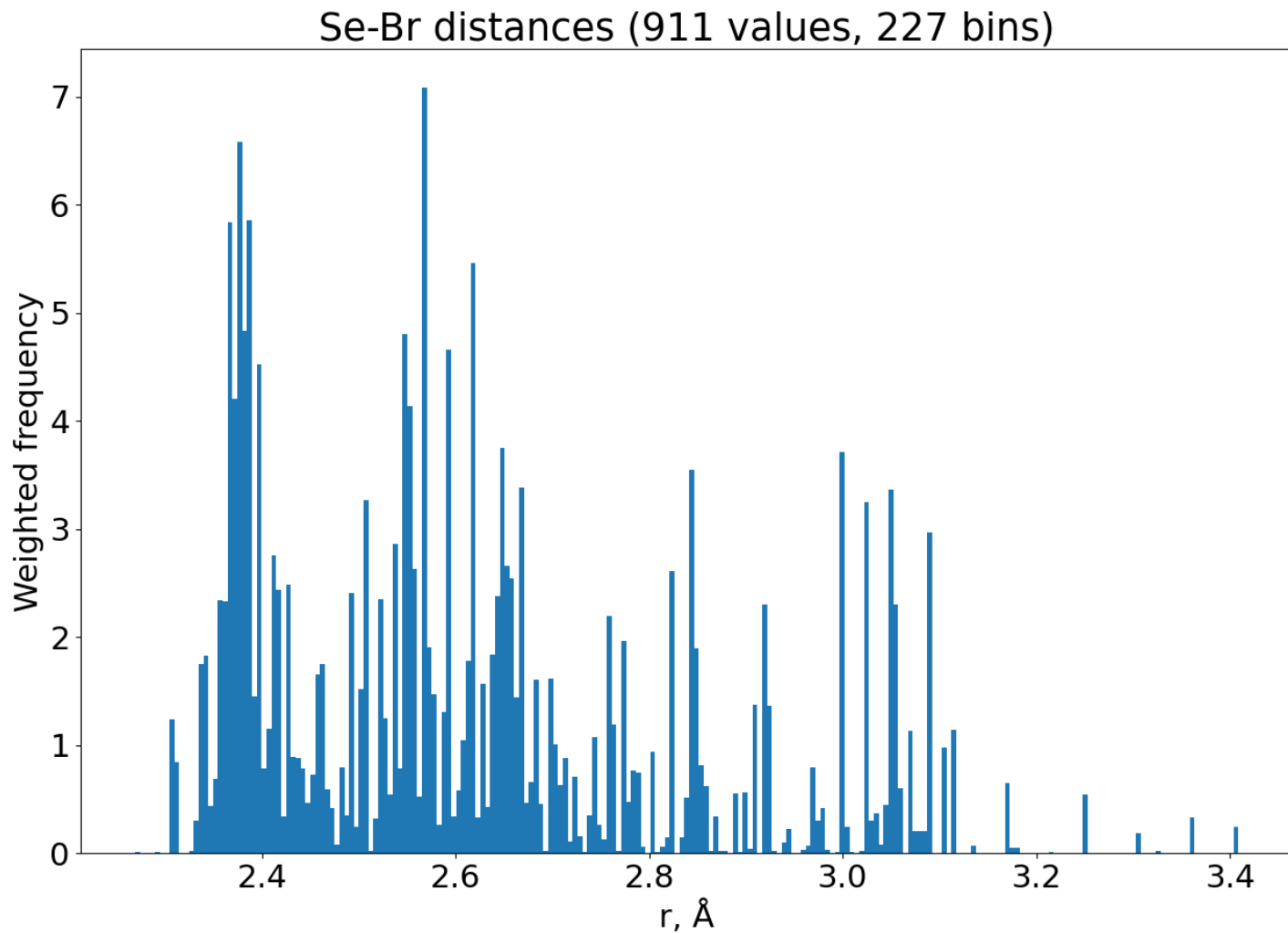
C-F distances (1039027 values, 345 bins)



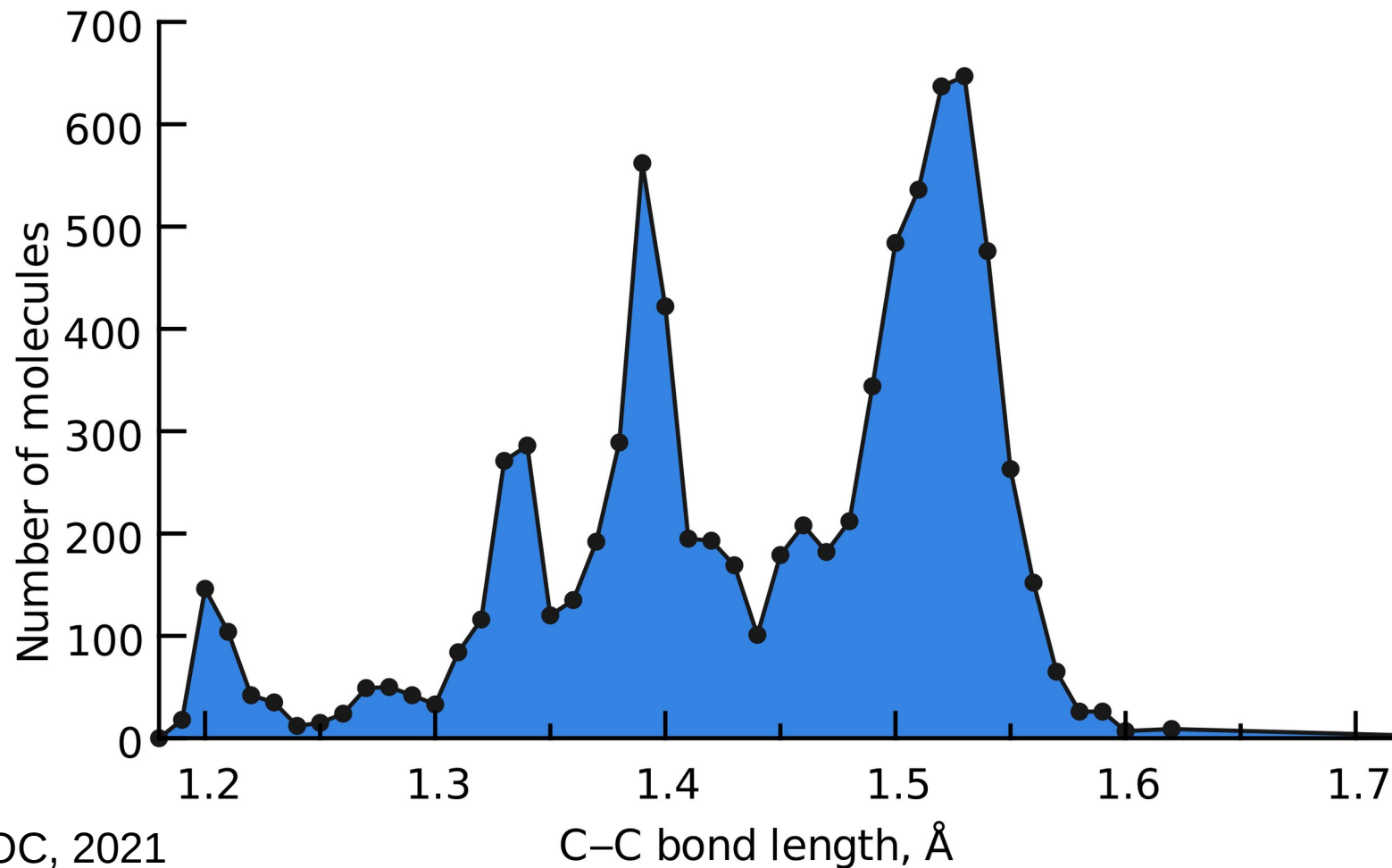
Осторожно, статистика в кристаллах!

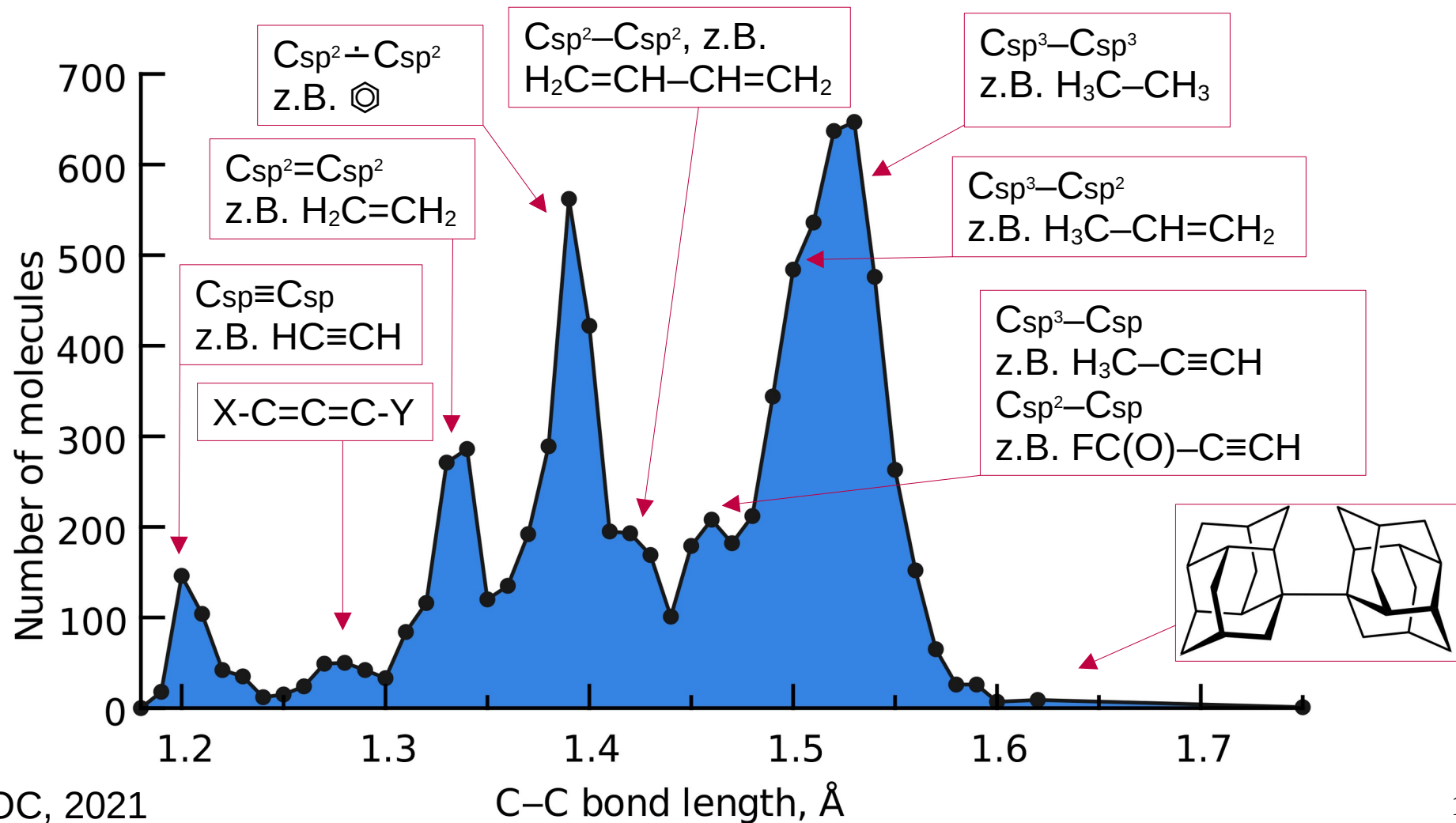


Осторожно, статистика в кристаллах!

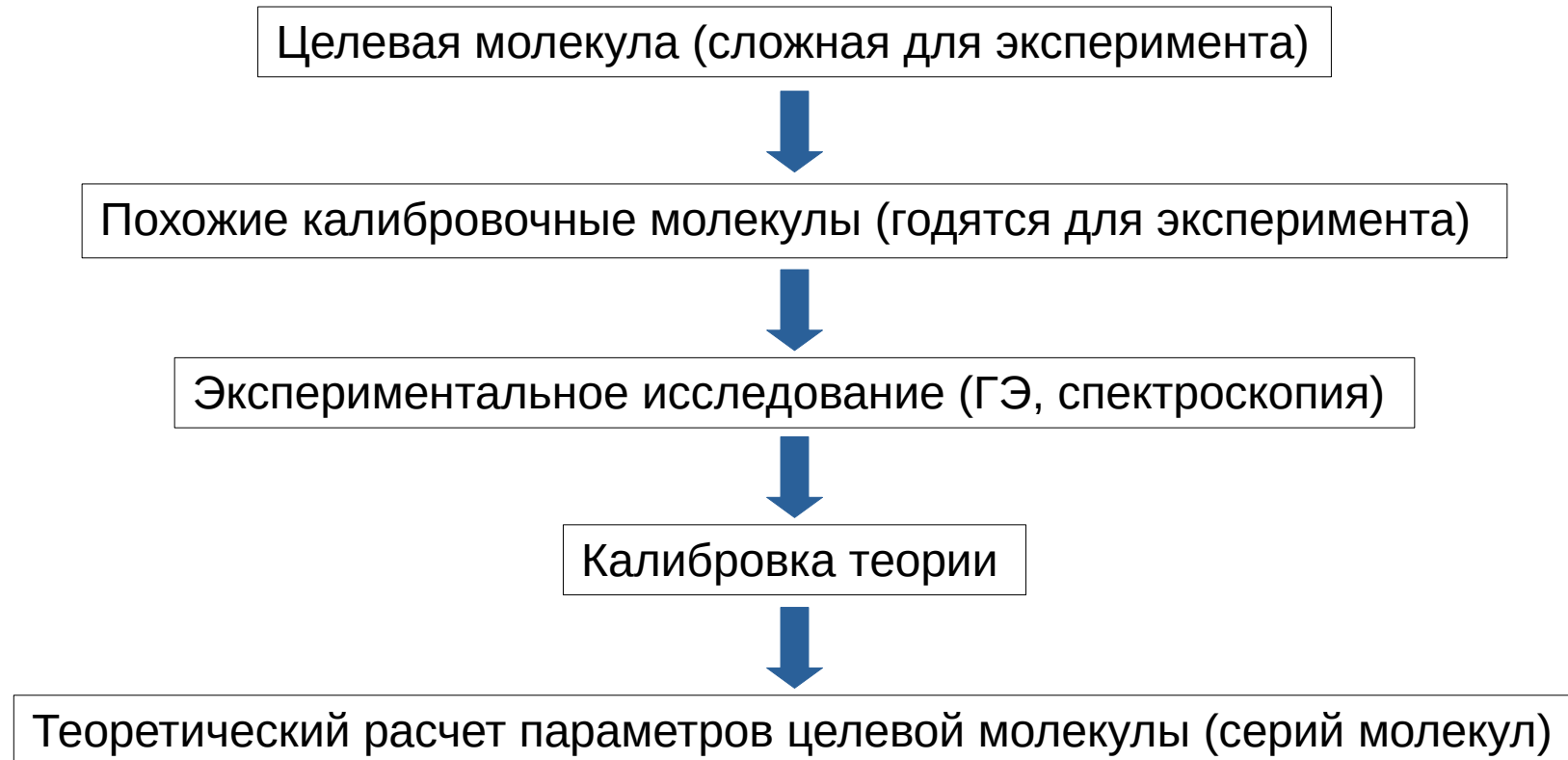


$r(\text{C}-\text{C})$: Эксперименты в газовой фазе





Рабочая схема исследования свободных молекул



Пример полезного ГЭ-исследования

Chalcogen Bonding

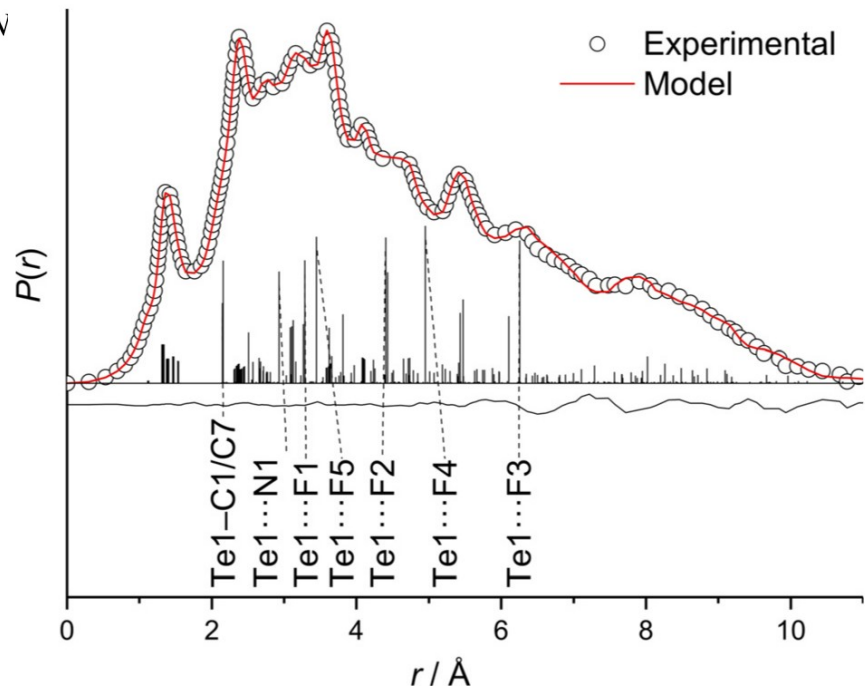
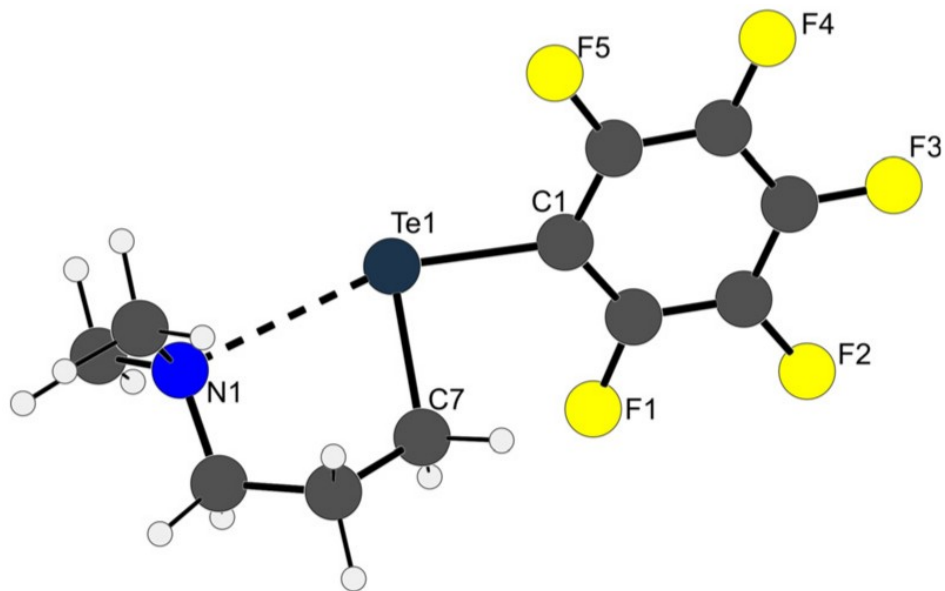
How to cite: *Angew. Chem. Int. Ed.* **2021**, *60*, 1519–1523

International Edition: doi.org/10.1002/anie.202013480

German Edition: doi.org/10.1002/ange.202013480

The Nature of Chalcogen-Bonding-Type Tellurium–Nitrogen Interactions: A First Experimental Structure from the Gas Phase

Timo Glodde, Yury V. Vishnevskiy, Lars Zimmermann, Hans-Georg Stammler, Beate N and Norbert W. Mitzel*



1. Делаем
интересное ГЭ



GDCh **Communications** *Angewandte*
International Edition *Chemie*

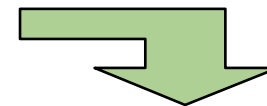
Chalcogen Bonding

How to cite: *Angew. Chem. Int. Ed.* **2021**, *60*, 1519–1523
International Edition: doi.org/10.1002/anie.202013480
German Edition: doi.org/10.1002/ange.202013480

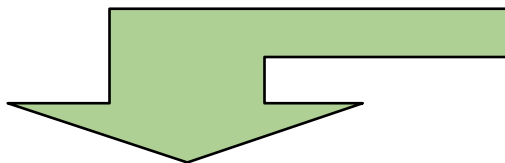
The Nature of Chalcogen-Bonding-Type Tellurium–Nitrogen Interactions: A First Experimental Structure from the Gas Phase

*Timo Glodde, Yury V. Vishnevskiy, Lars Zimmermann, Hans-Georg Stammler, Beate Neumann, and Norbert W. Mitzel**

2. Теоретики
возбуждаются



3. Перепроверяем ГЭ



GDCh **Correspondence** *Angewandte*
International Edition *Chemie*

Computational Chemistry

How to cite: *Angew. Chem. Int. Ed.* **2021**, *60*, 13144–13149
International Edition: doi.org/10.1002/anie.202102679
German Edition: doi.org/10.1002/ange.202102679

Comment on “The Nature of Chalcogen-Bonding-Type Tellurium–Nitrogen Interactions”: Fixing the Description of Finite-Temperature Effects Restores the Agreement Between Experiment and Theory

Jan-Michael Mewes, Andreas Hansen, and Stefan Grimme*

GDCh **Correspondence** *Angewandte*
International Edition *Chemie*

Gas-Phase Structures

How to cite: *Angew. Chem. Int. Ed.* **2021**, *60*, 13150–13157
International Edition: doi.org/10.1002/anie.202104899
German Edition: doi.org/10.1002/ange.202104899

Reply to a Comment on “The Nature of Chalcogen-Bonding-Type Tellurium–Nitrogen Interactions”

*Yury V. Vishnevskiy and Norbert W. Mitzel**

4. Уточняем теорию



Применение теории

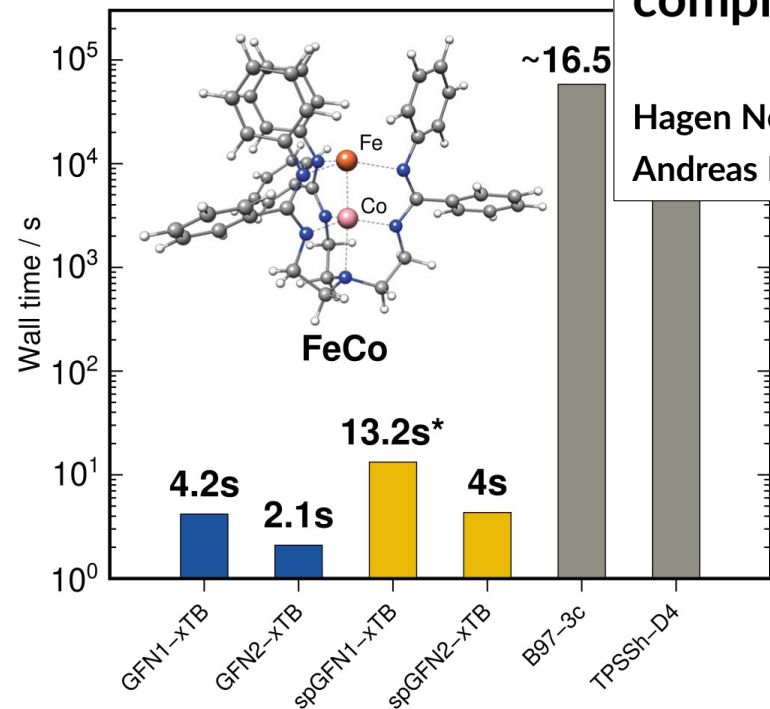
DOI: 10.1002/jcc.27185

RESEARCH ARTICLE

Journal of
COMPUTATIONAL
CHEMISTRY WILEY

High-throughput screening of spin states for transition metal complexes with spin-polarized extended tight-binding methods

Hagen Neugebauer¹  | Benedikt Bädorf¹  | Sebastian Ehlert²  |
Andreas Hansen¹  | Stefan Grimme¹ 



Применение теории

Stannanes

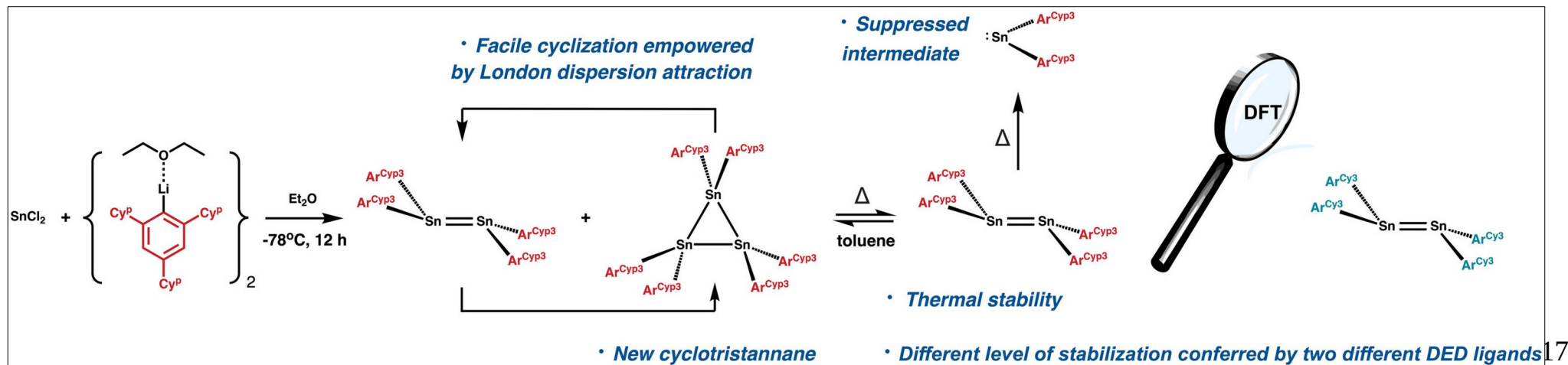
How to cite:

International Edition: doi.org/10.1002/anie.202301919

German Edition: doi.org/10.1002/ange.202301919

London Dispersion Effects in a Distannene/Tristannane Equilibrium: Energies of their Interconversion and the Suppression of the Monomeric Stannylene Intermediate

Wenxing Zou, Markus Bursch,* Kristian L. Mears, Cary R. Stennett, Ping Yu, James C. Fettinger, Stefan Grimme,* and Philip P. Power*



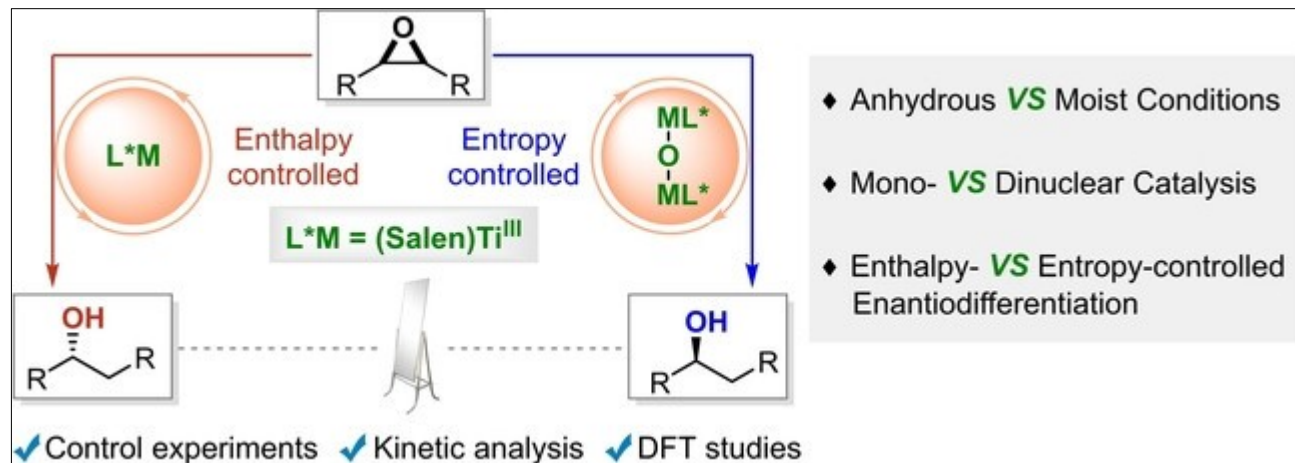
Применение теории

How to cite: *Angew. Chem. Int. Ed.* **2023**, 62, e202309525
doi.org/10.1002/anie.202309525

Asymmetric Catalysis

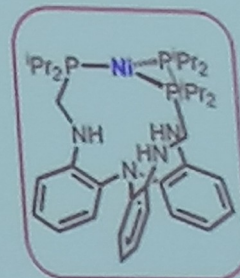
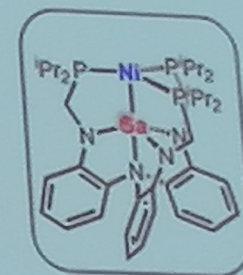
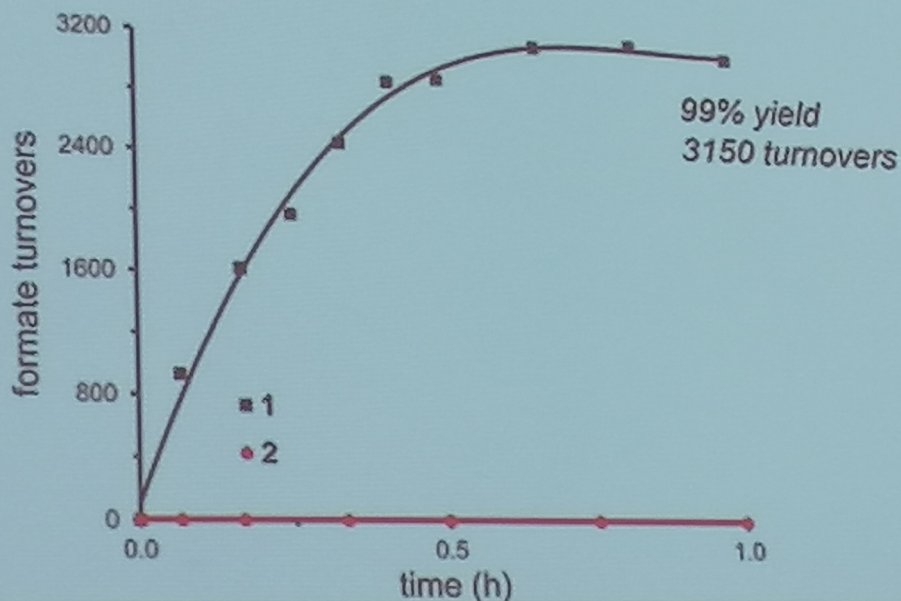
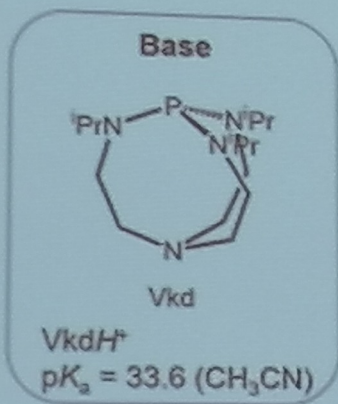
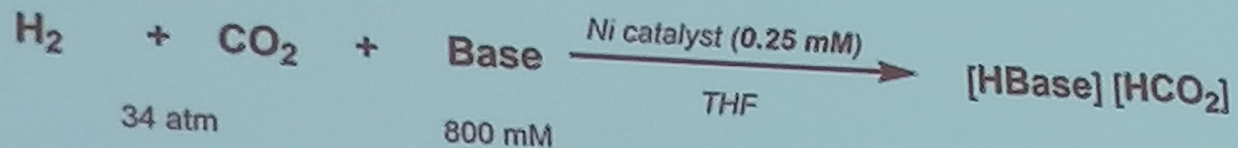
A Nuclearity-Dependent Enantiodivergent Epoxide Opening via Enthalpy-Controlled Mononuclear and Entropy-Controlled Dinuclear (Salen)Titanium Catalysis

Shengxiao Li, Hui Zhu, Longfei Li, Wanjiao Chen, Jie Jiang, Zheng-Wang Qu,*
Stefan Grimme, and Yong-Qiang Zhang*



Важность теории: Recent Advances in Lewis-acid Chemistry

Catalytic CO₂ hydrogenation using the Ni-Ga catalyst



Длинные С–С связи

Overcoming lability of extremely long alkane carbon–carbon bonds through dispersion forces

Peter R. Schreiner¹, Lesya V. Chernish², Pavel A. Gunchenko², Evgeniya Yu. Tikhonchuk², Heike Hausmann¹, Michael Serafin³, Sabine Schlecht³, Jeremy E. P. Dahl⁴, Robert M. K. Carlson⁴ & Andrey A. Fokin^{1,2}

J | A | C | S
JOURNAL OF THE AMERICAN CHEMICAL SOCIETY

Article

pubs.acs.org/JACS

Chem

Article

Longest C–C Single Bond among Neutral Hydrocarbons with a Bond Length beyond 1.8 Å

Yusuke Ishigaki,^{1,*} Takuya Shimajiri,¹ Takashi Takeda,^{1,2} Ryo Katoono,¹ and Takanori Suzuki^{1,3,*}

Stable Alkanes Containing Very Long Carbon–Carbon Bonds

Andrey A. Fokin,^{*,1,‡} Lesya V. Chernish,¹ Pavel A. Gunchenko,¹ Evgeniya Yu. Tikhonchuk,¹ Heike Hausmann,[‡] Michael Serafin,[§] Jeremy E. P. Dahl,^{||} Robert M. K. Carlson,^{||} and Peter R. Schreiner^{*,‡}

Long Carbon–Carbon Bonding beyond 2 Å in Tris(9-fluorenylidene)methane

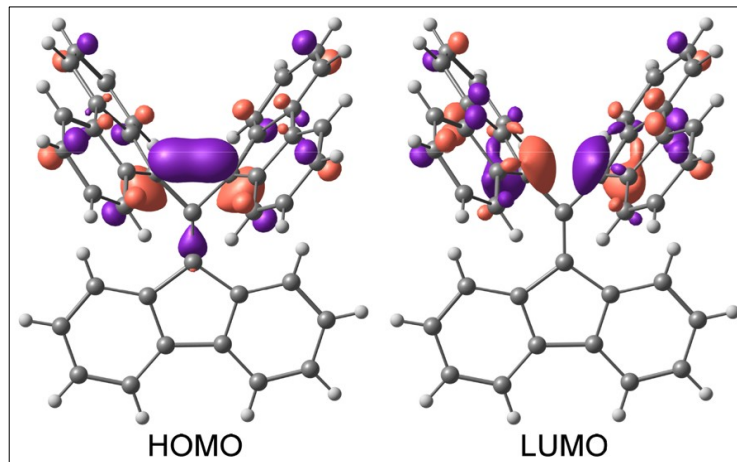
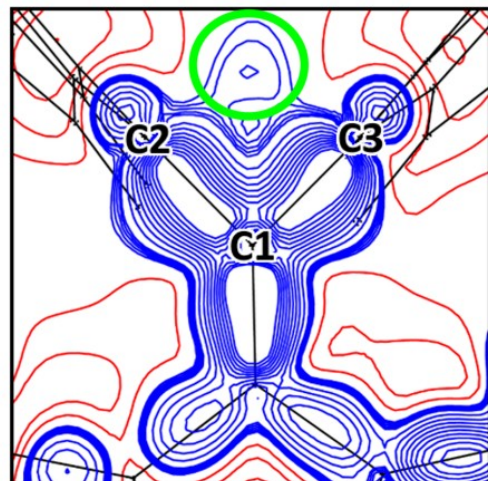
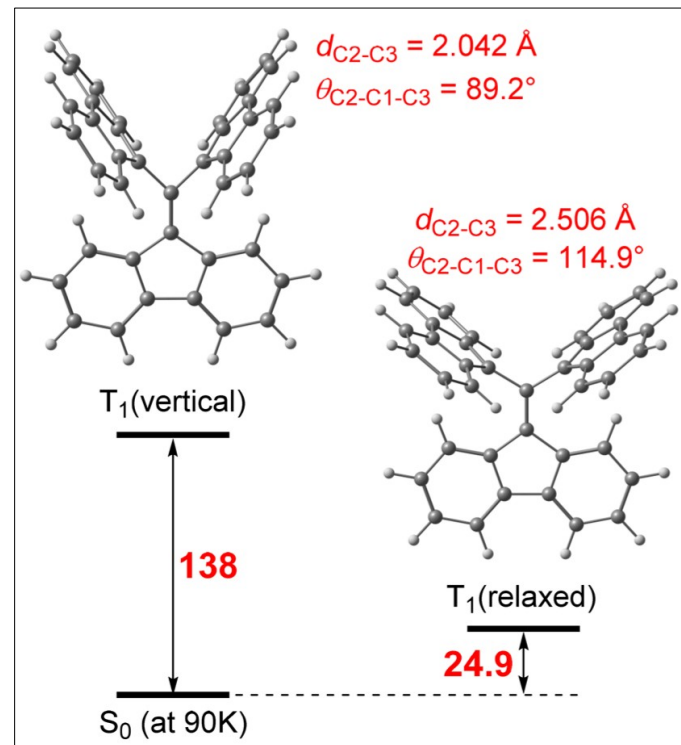
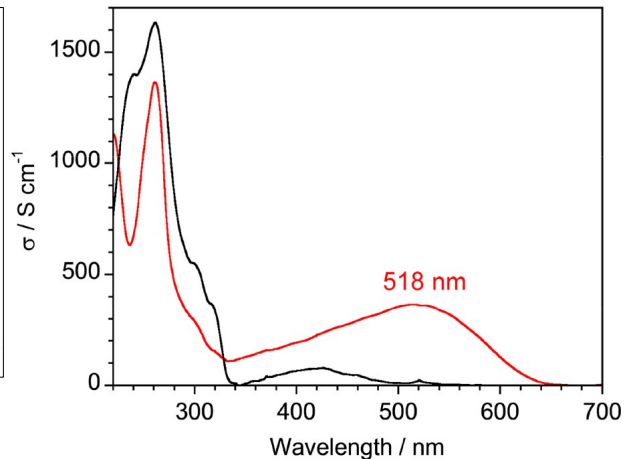
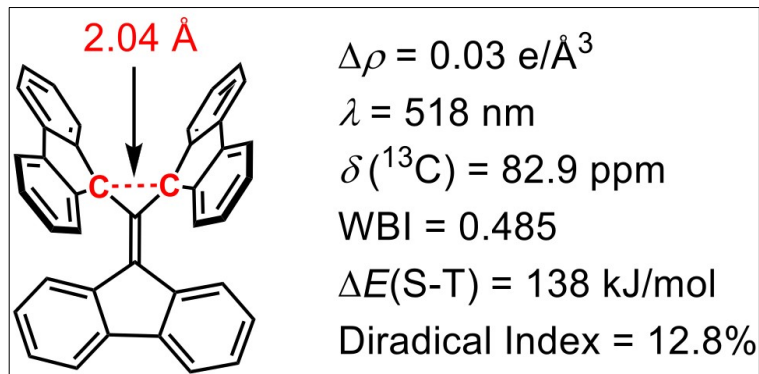
Takashi Kubo,^{*} Yuki Suga, Daisuke Hashizume,^{*} Hiroki Suzuki, Tatsuya Miyamoto, Hiroshi Okamoto, Ryohei Kishi, and Masayoshi Nakano



Cite This: *J. Am. Chem. Soc.* 2021, 143, 14360–14366

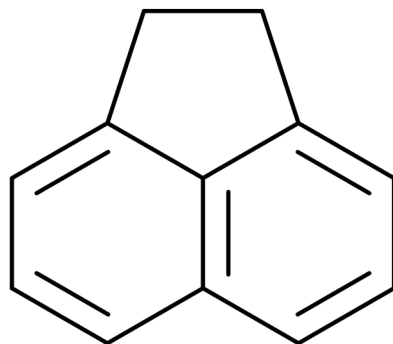


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B3LYP-D3/6-311+G**

Аценафтен: наше ГЭ исследование



PCCP

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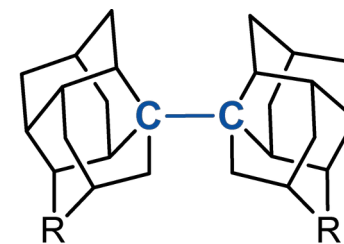
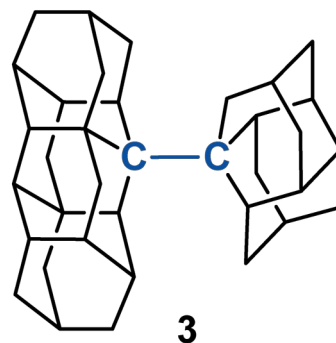
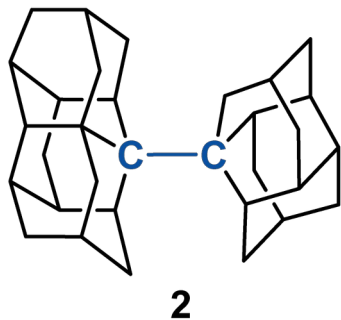
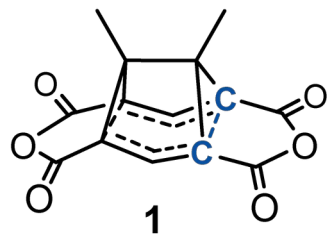


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Cite this: *Phys. Chem. Chem. Phys.*,
2023, 25, 11464

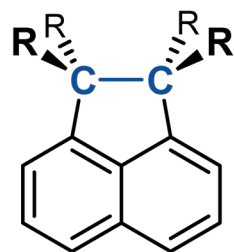
Accurate single crystal and gas-phase molecular structures of acenaphthene: a starting point in the search for the longest C–C bond†

Yury V. Vishnevskiy, *^a Arseniy A. Otlyotov, ^b Jan-Hendrik Lamm, ^a
Hans-Georg Stammer, ^a Georgiy V. Girichev^c and Norbert W. Mitzel *^a



R = CH₂ (4a)

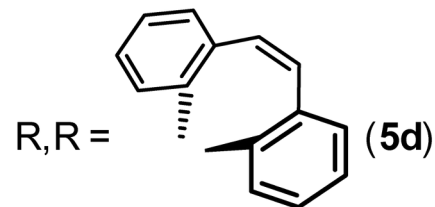
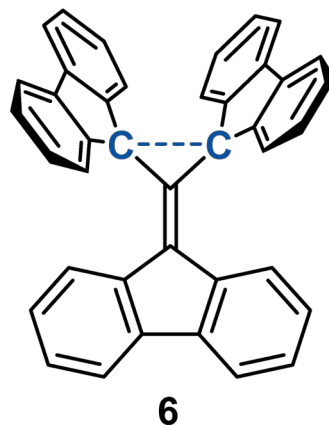
R = O (4b)



R = H (5a) – *this work*

R = 4-*t*-Bu-C₆H₄ (5b)

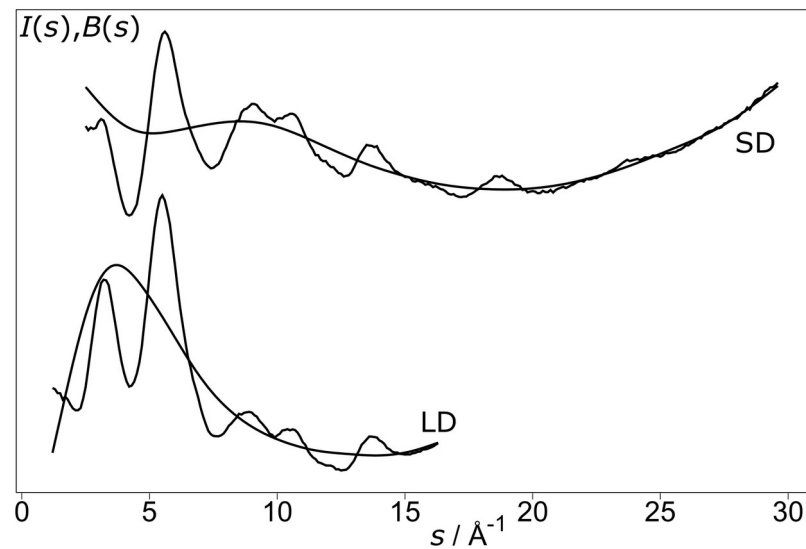
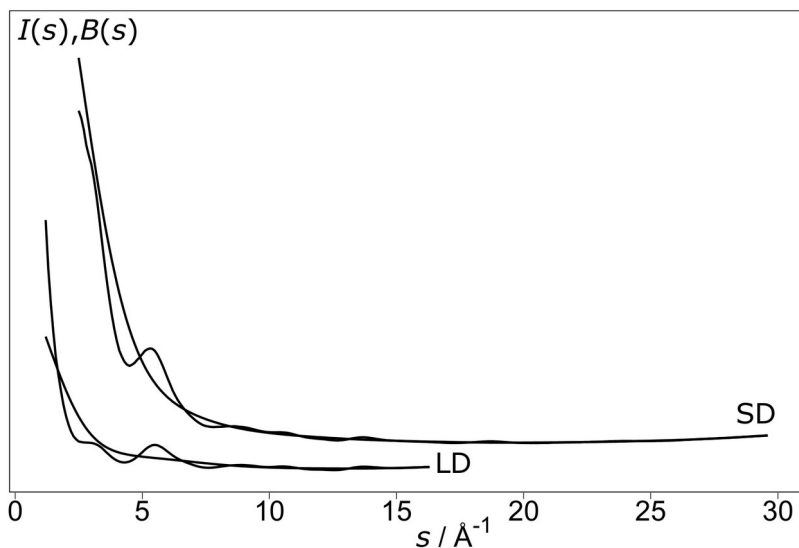
R = C₆H₅ (5c)



	Кристалл	Газ
	$d(\text{C}-\text{C})$ (s) [Å]	$d(\text{C}-\text{C})$ (g) [Å]
1	1.670(1)	1.737(44)
2	1.704(4)	n.a.
3	1.71	n.a.
4a	1.647(4)	1.630(5)
4b	1.642(2)	1.632(5)
5a		
5b	1.708(4)	n.a.
5c	1.701(3)	n.a.
5d	1.746(3)	n.a.
6	2.0415(5)	n.a.

ГЭ линии фона

Модифицирующая функция: $f(s) = y_r \left[1 + \left(\frac{y_i - y_r}{y_r} \right) \times (1 + \exp(s - s_0)/\Delta s)^{-1} \right]$

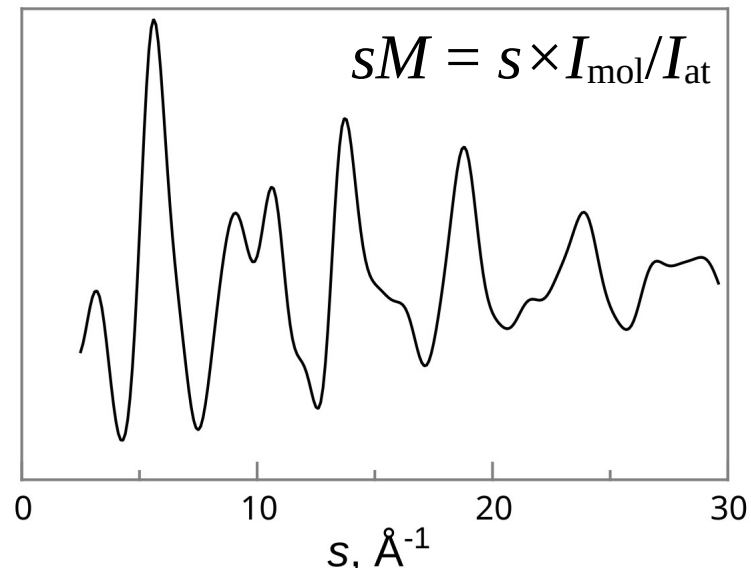
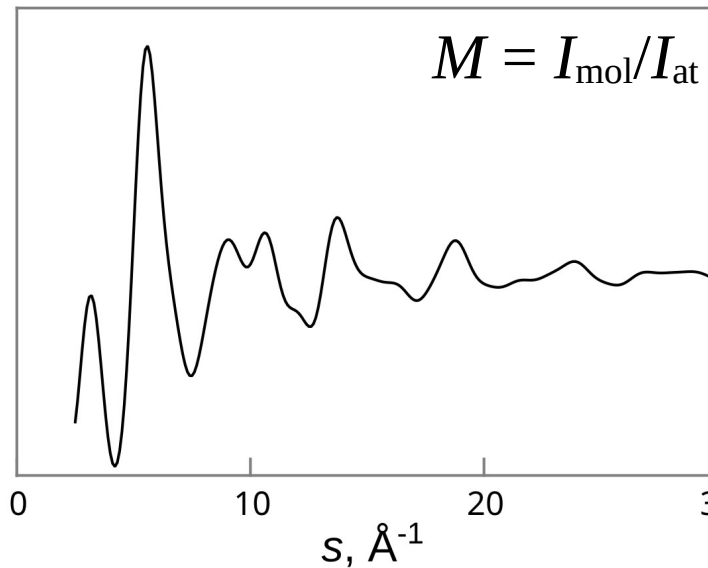
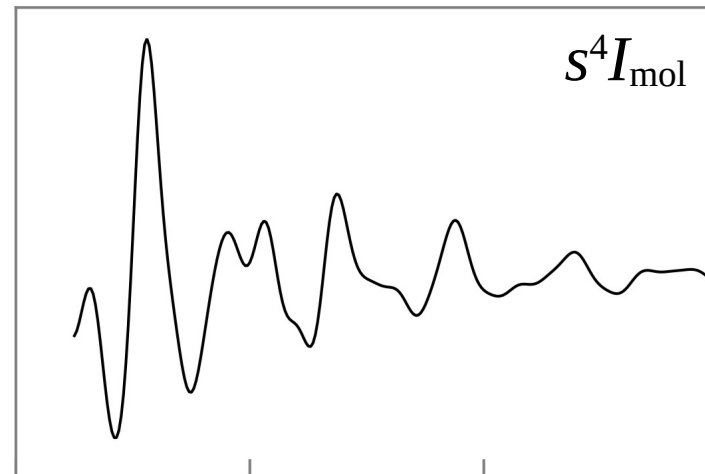
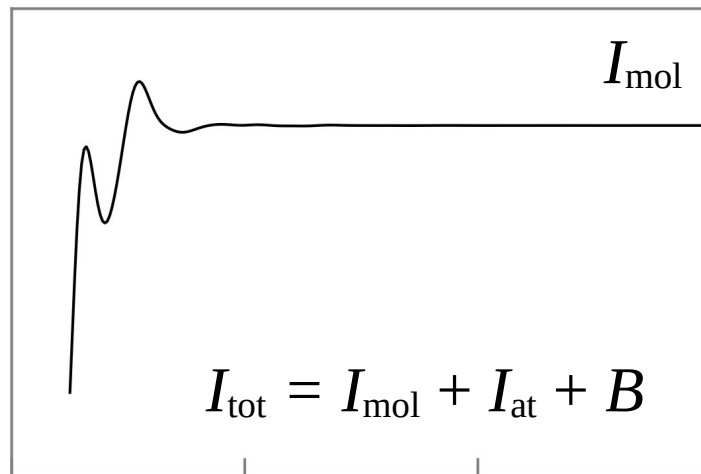


Вторая производная, как критерий гладкости:

Неприменима

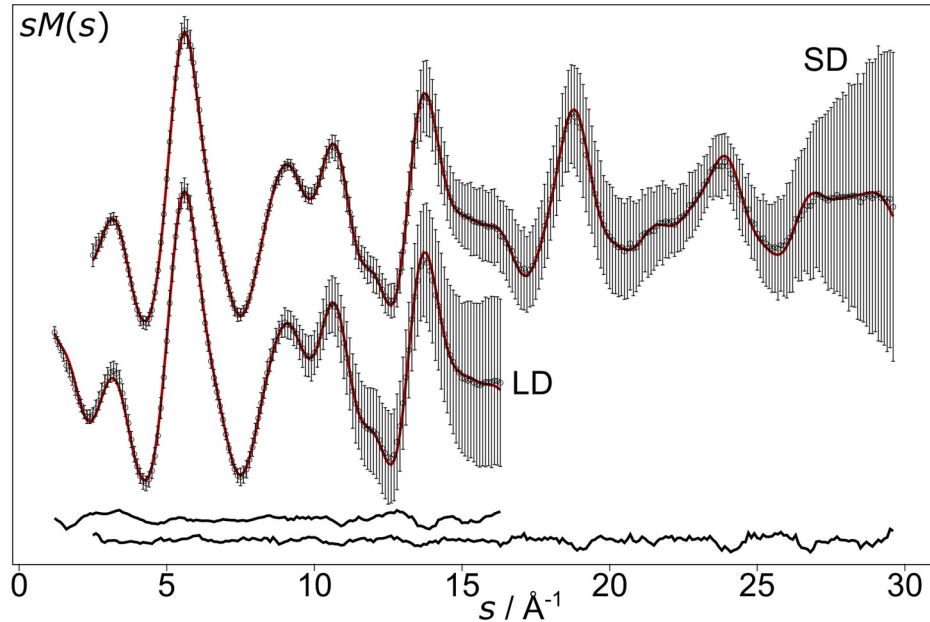
Применима

Какую молекулярную функцию выбрать?

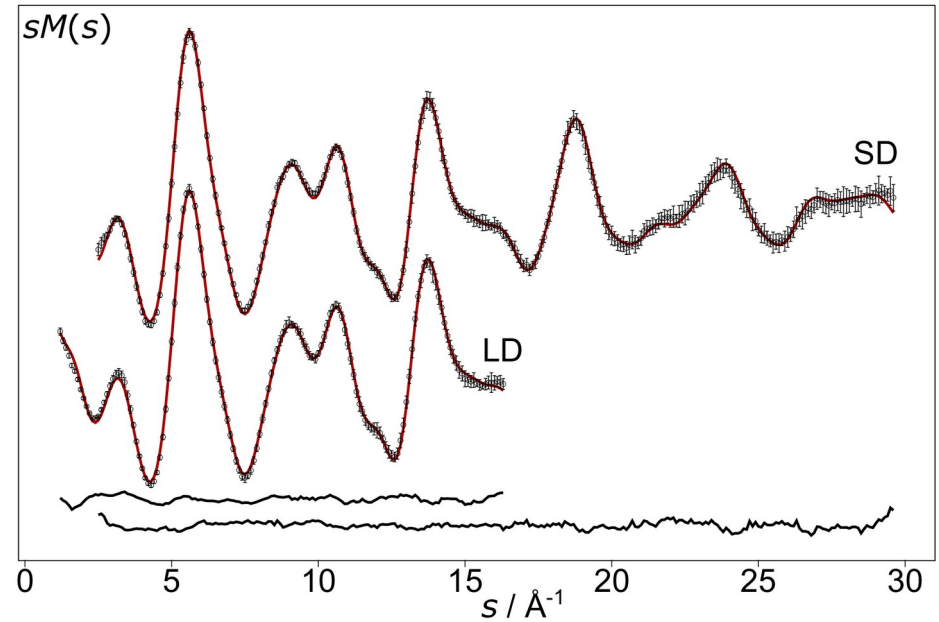


Веса экспериментальных интенсивностей

$$Q = \sum_i^L w_{(\text{GED}),i} \left[sM(s)_{(e),i} - sM(s)_{(m),i} \right]^2 \quad w_{(\text{GED})} = \sigma_{\text{SM}}^{-2} \quad sM(s) = \frac{I(s) - \Phi(s)}{\Phi(s)} \times s \quad \sigma_{\text{SM}} = \frac{\sigma_I}{\Phi(s)} \times s$$

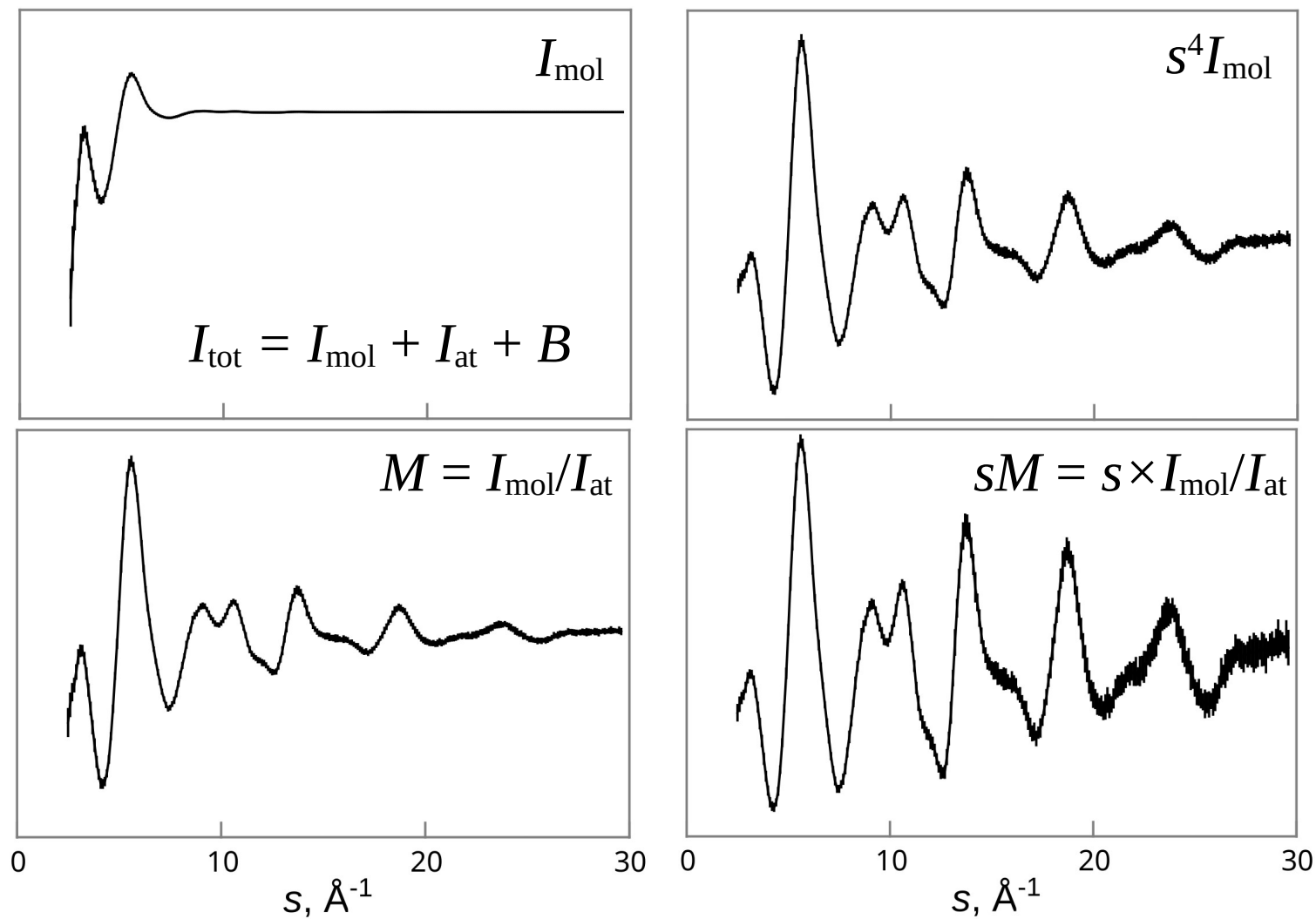


Усреднение полных интенсивностей.
Очень низкая прецизионность
молекулярной интенсивности!

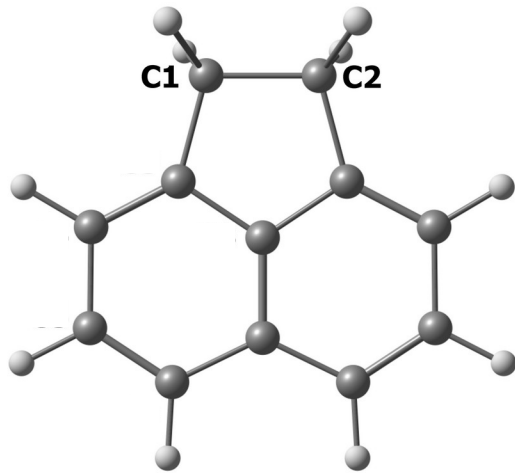


Усреднение молекулярных интенсивностей.
Высокая прецизионность!

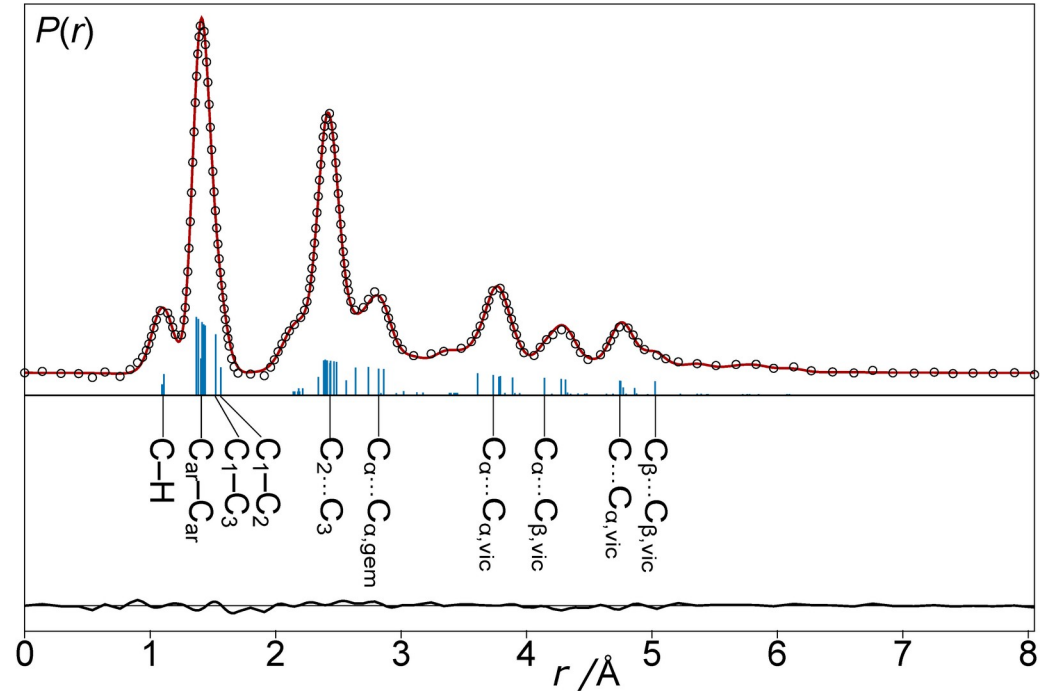
С честными ст. отклонениями все варианты эквивалентны



$r(\text{C}-\text{C})$ в аценафтене

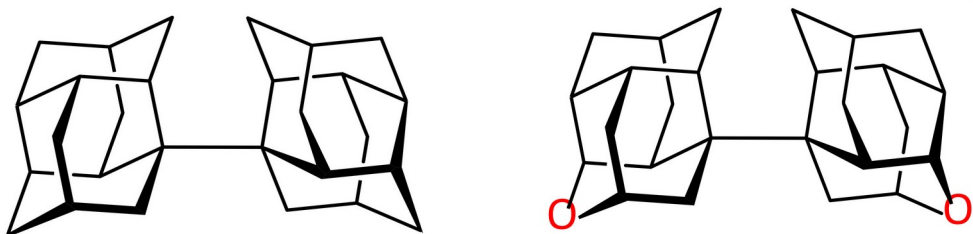


Метод	$r_e(\text{C1}-\text{C2}), \text{\AA}$
ГЭ+МВ	1.560(4)
РСА	1.5640(4)
CCSD(T)	1.562
r^2 SCAN-3c	1.564
PBEh-3c	1.556



Димеры диамантана

Источник экспериментальных данных для калибровки теоретических приближений.

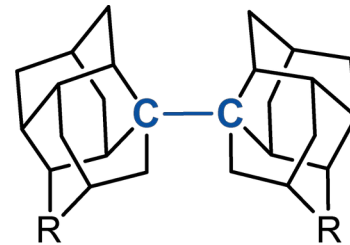
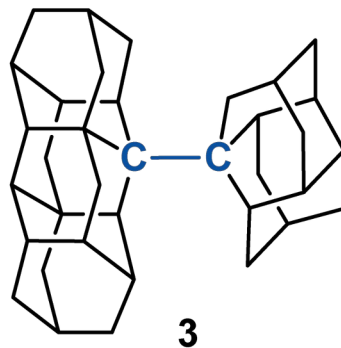
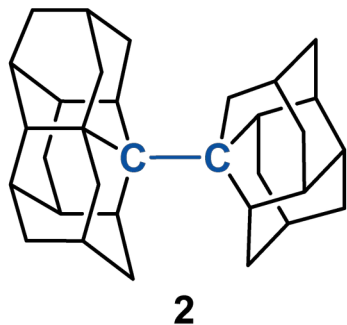
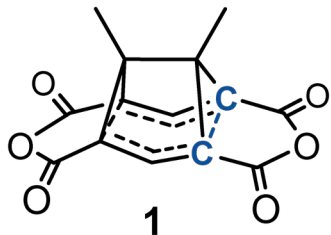


В этом исследовании ключевую роль играет газовая электронография!

A. A. Fokin, T. S. Zhuk, S. Blomeyer, C. Pérez, L. V. Chernish, A. E. Pashenko, J. Antony, Y. V. Vishnevskiy, R. J. F. Berger, S. Grimme, C. Logemann, M. Schnell, N. W. Mitzel, P. R. Schreiner, "Intramolecular London Dispersion Interaction Effects on Gas-Phase and Solid-State Structures of Diamondoid Dimers", *J. Am. Chem. Soc.* 139 (2017) 16696.

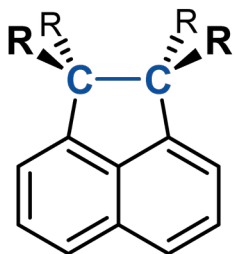
Метод	О-Димер	Димер
РСА	1.643(1)	1.647(4)
ГЭ	1.632(9)	1.630(5)
ГЭ+МВ	1.632(5)	-
B3LYP/cc-pVTZ	1.662	1.674
TPSS/cc-pVTZ	1.658	1.668
HF/cc-pVTZ	1.652	1.664
B97-D3/cc-pVTZ	1.651	1.662
r²SCAN-3c	1.645	1.655
TPSS-D3/cc-pVTZ	1.642	1.652
B3LYP-D3/cc-pVTZ	1.642	1.653
ω B97XD/cc-pVTZ	1.638	1.648
PBE0/cc-pVTZ	1.637	1.648
M06-2X/cc-pVTZ	1.636	1.647
PBEh-3c	1.632	1.642
SCS(1.2;2/3)-MP2/def2-QZVP	1.629	1.640
PBE0-D3/cc-pVTZ	1.628	1.638
B3PW91-D3/cc-pVTZ	1.627	1.636
PW6B95-D3/def2-QZVP	1.626	1.636
ae-MP2/cc-pwCVTZ	1.622	1.633

Используем теорию:



R = CH₂ (**4a**)

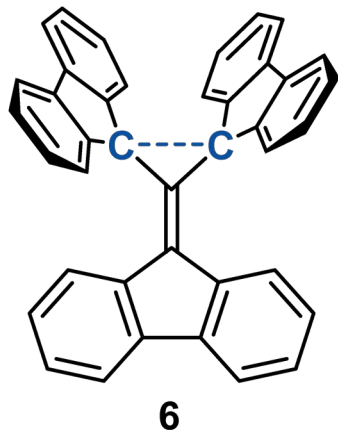
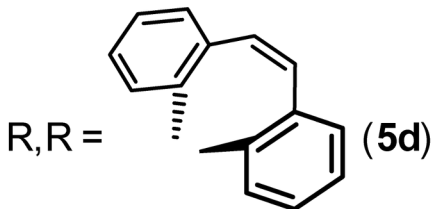
R = O (**4b**)



R = H (**5a**) – *this work*

R = 4-*t*-Bu-C₆H₄ (**5b**)

R = C₆H₅ (**5c**)



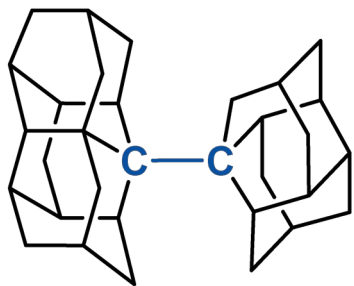
	Кристалл $d(\text{C}-\text{C})$ (s) [Å]	Газ $d(\text{C}-\text{C})$ (g) [Å]	
1	1.670(1)	1.737(44)	[1.633]
2	1.704(4)	[1.686]	
3	1.71	[1.694]	
4a	1.647(4)	1.630(5)	
4b	1.642(2)	1.632(5)	
5a	1.5640(4)	1.560(4)	[PBEh-3c]
5b	1.708(4)	[1.680]	
5c	1.701(3)	[1.678]	
5d	1.746(3)	[1.704]	
6	2.0415(5)	[1.653]	

Кристаллическая структура 6

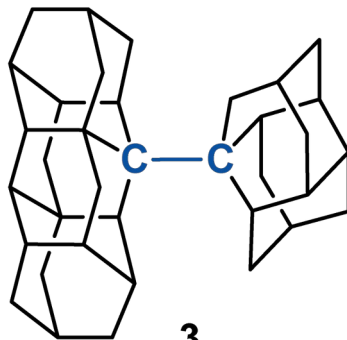
CSD: UREGOQ



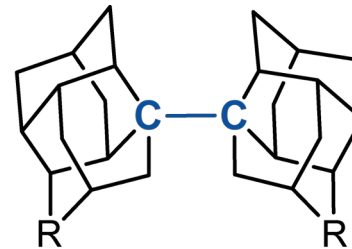
Предсказываем
возможные
варианты
расчетами
фторзамещенных
аналогов:



2

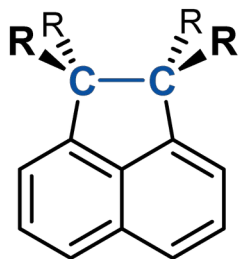


3



R = CH₂ (4a)

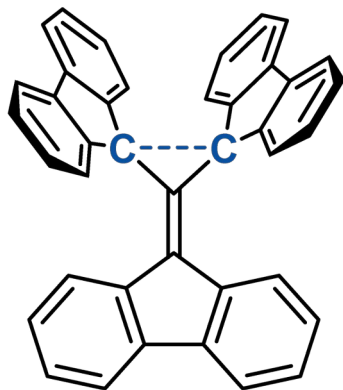
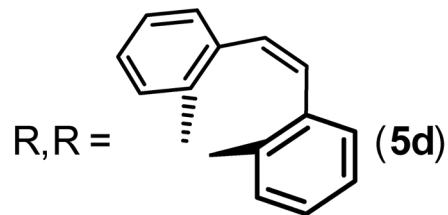
R = O (4b)



R = H (5a) – *this work*

R = 4-*t*-Bu-C₆H₄ (5b)

R = C₆H₅ (5c)



6

Кристалл
 $d(\text{C}-\text{C})$ (s) [Å]

Газ
 $d(\text{C}-\text{C})$ (g) [Å]

Газ
 $d(\text{C}-\text{C})$ (g) [Å]
Фтор-замещ.

2 1.704(4)

[1.686]

[3.918]**

3 1.71

[1.694]

[3.936]**

4a 1.647(4)

1.630(5)

[2.417]*

4b 1.642(2)

1.632(5)

[2.168]*

5a 1.5640(4)

1.560(4)

[1.584]

5b 1.708(4)

[1.680]

[1.700]

5c 1.701(3)

[1.678]

[1.725]

5d 1.746(3)

[1.704]

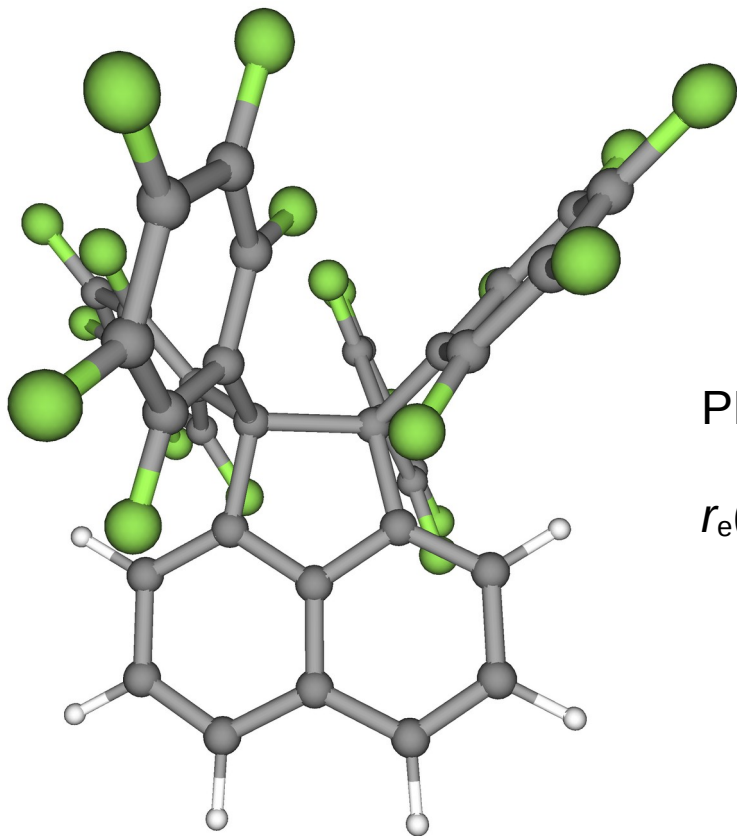
[1.691]

6 2.0415(5)

[1.653]

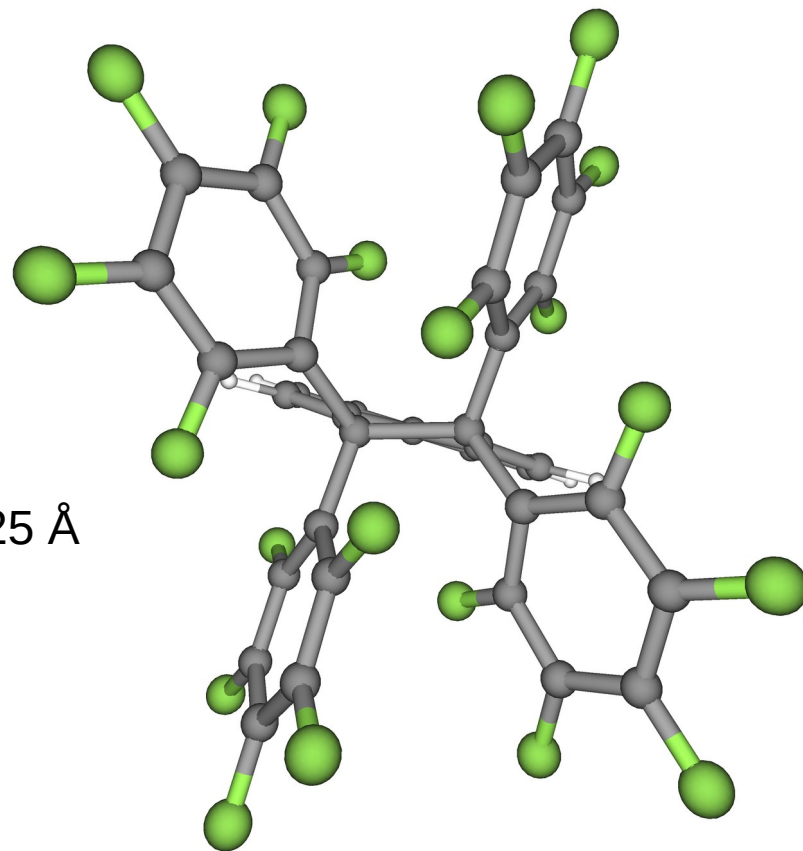
[1.691]

Предсказание для **5c** при R = C₆F₅



PBEh-3c:

$$r_e(\text{C—C}) = 1.725 \text{ \AA}$$



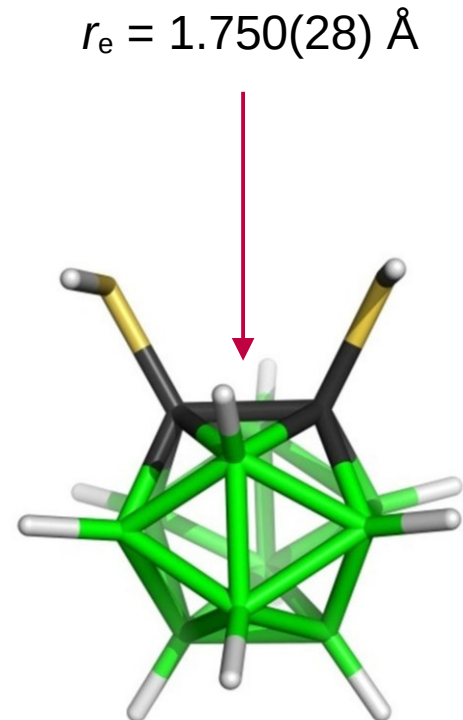
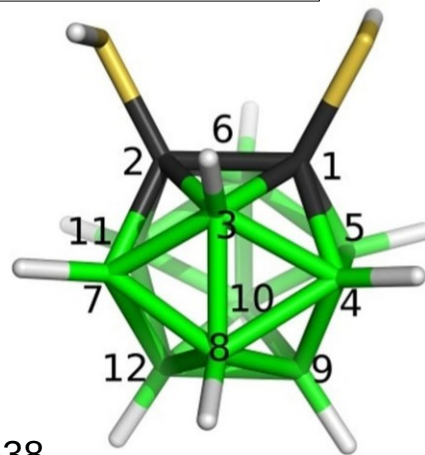
Другие варианты с длинной C—C

Carboranes

Icosahedral Carboranes with Peripheral Hydrogen–Chalcogenide Groups: Structures from Gas Electron Diffraction and Chemical Shielding in Solution

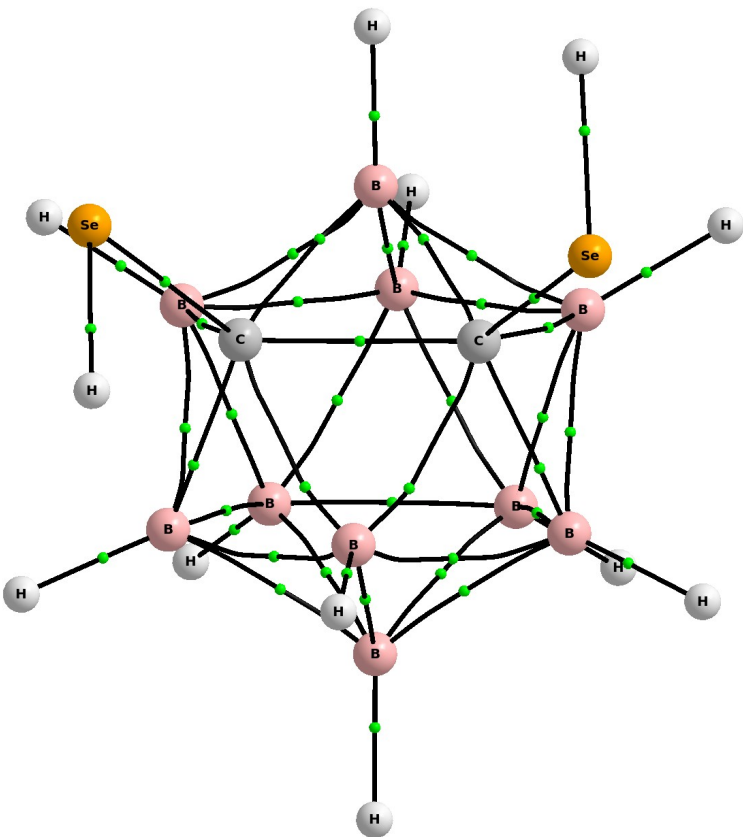
Tomáš Baše,^[a] Josef Holub,^[a] Jindřich Fanfrlík,^[b] Drahomír Hnyk,^{*,[a]} Paul D. Lane,^[c, d] Derek A. Wann,^[c] Yury V. Vishnevskiy,^{*,[e]} Denis Tikhonov,^[e, f, g] Christian G. Reuter,^[e] and Norbert W. Mitzel^{*,[e]}

1,2-(EH)₂-клозо-1,2-C₂B₁₀H₁₀, E = S, Se

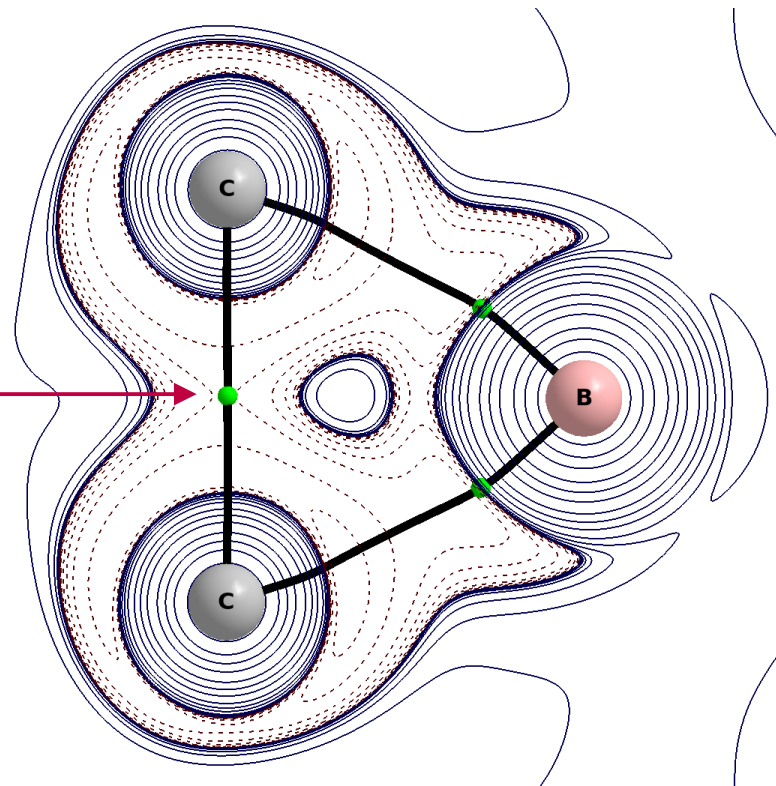


QTAIM указывает на наличие связи

1,2-(SeH)₂-клозо-1,2-C₂B₁₀H₁₀



$\rho = 0.16 \text{ a.e.}$
 $\Delta\rho = -0.08 \text{ a.e.}$



Выводы

- Заявленное Kibo с соавторами $r(\text{C}-\text{C}) = 2.04 \text{ \AA}$ крайне сомнительно для свободной молекулы. Это параметр кристалла!
- У молекул на основе аценафтена есть потенциал для удлинения C–C связи путём использования перфторзамещенных групп.
- Газовая электронография — незаменимый источник экспериментальных данных о геометрии свободных больших молекул.
- Делать расчеты можно и нужно, но для этого необходимо калибровать теорию.
- Давайте выбирать для экспериментальных исследований максимально полезные объекты (смотри карту связей).
- Если результаты экспериментального исследования полностью совпали с предсказанием, то ценность такой работы невелика.