Теоретические основы органической химии

Соединения с инвертированной геометрией

Лекция 4
(мультимедийный курс)

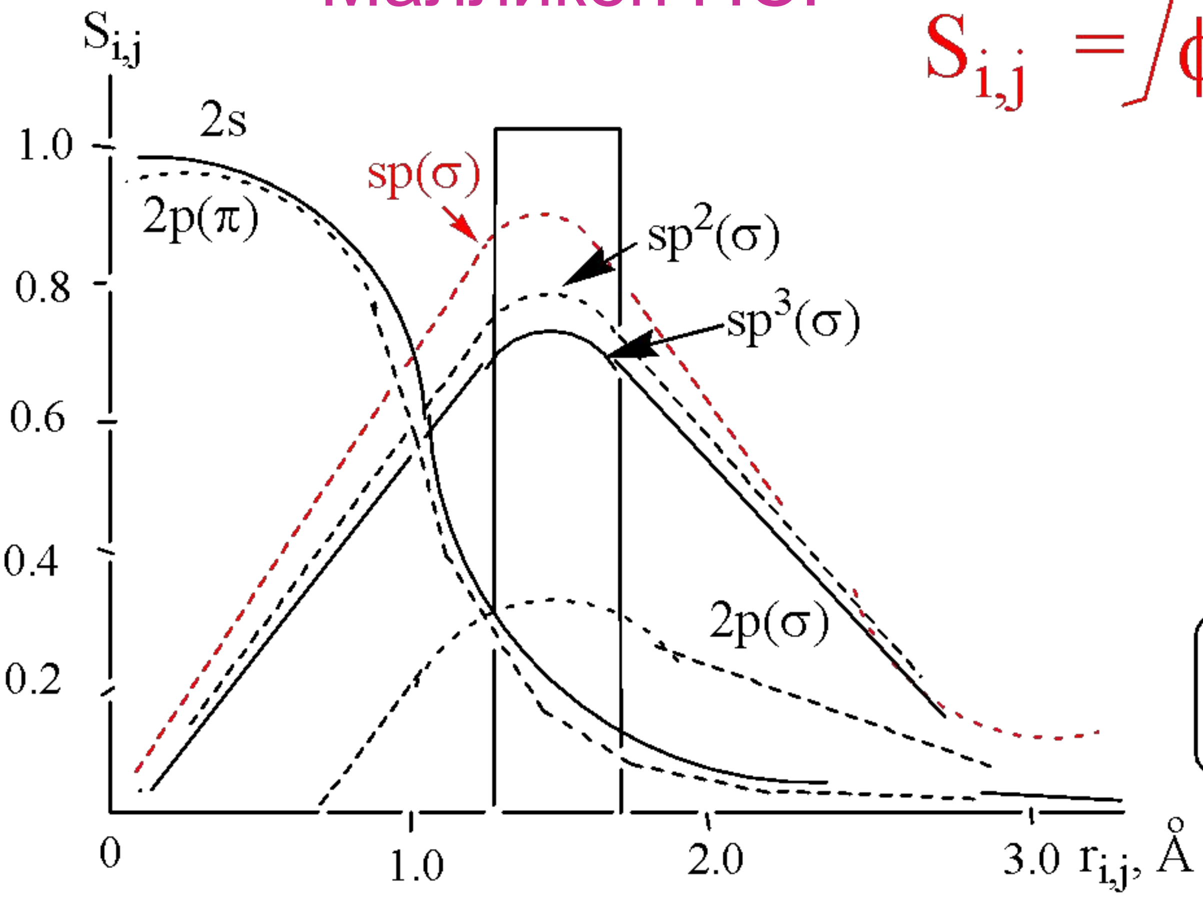
Проф. Бородкин Г.И.

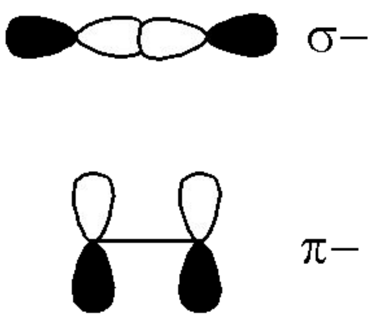
Теория гибридизации

1. Направленность орбиталей
2. Принцип максимального орбитального перекрывания

Малликен Р.С.

$$S_{i,j} = \int \phi_i \phi_j \, d\tau$$





$sp^3 < sp^2 < sp$

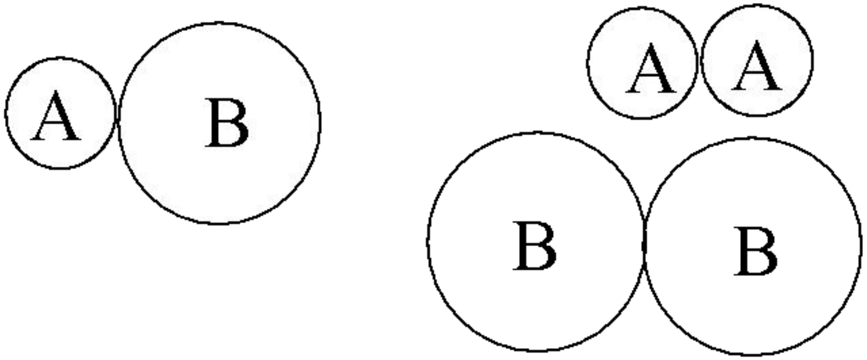
Молекула	Гибридизация	E_{C-H}, ккал/моль	l_{C-H}, Å
CH_3-CH_3	sp^3	97	1.094
$CH_2=CH_2$	sp^2	104	1.084
$CH\equiv CH$	sp	114	1.061

ПМП !

прочность связи ↓

укорочение ↓

Ковалентный радиус



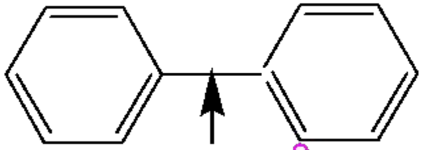
$$r_A = 1/2\, l_{A-A}$$

$$r_B = 1/2\, l_{B-B}$$

Аддитивная схема

1.54 Å

$CH_3{-}CH_3$



1.49 Å

$RC{\equiv}CR$

1.38 Å

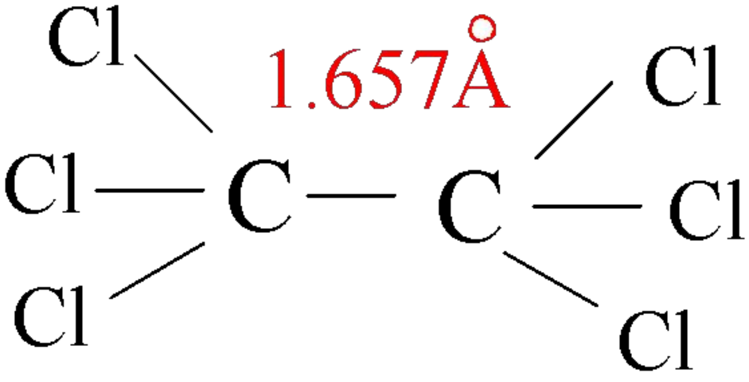
$$r^{C}_{sp^3} = 1.54/2 = 0.77\ \text{Å}$$

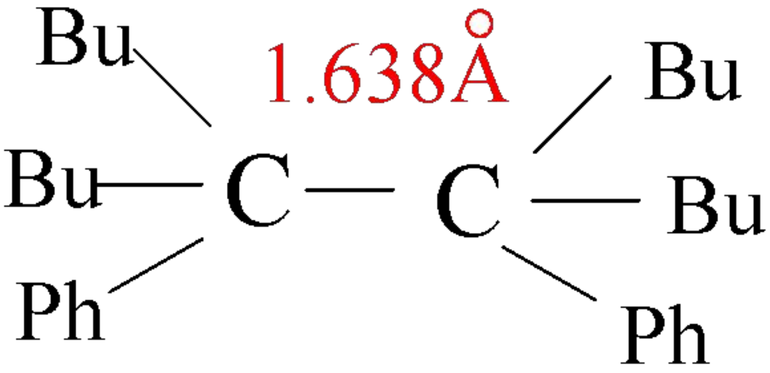
$$r^{C}_{sp^2} = 1.49/2 = 0.745\ \text{Å}$$

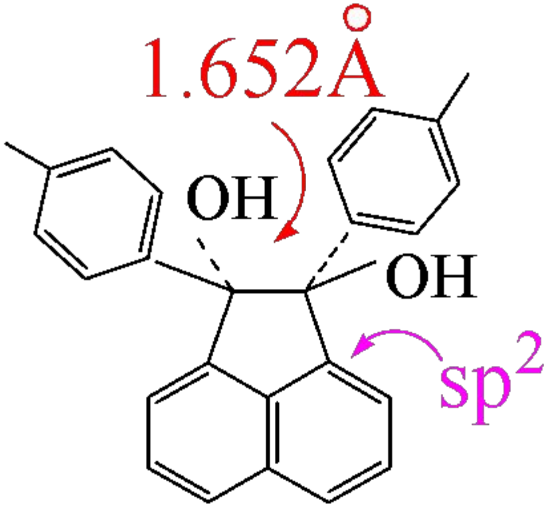
$$r^{C}_{sp} = 1.38/2 = 0.69\ \text{Å}$$

	$H_3C{-}CH{=}CH_2$	$H_3C{-}C{\equiv}CH$	$H_3C{-}C{\equiv}N$	$Ph{-}C{\equiv}C{-}Ph$
	⇧	⇧	⇧	⇧
расчет	1.51	1.46	1.46	1.43 Å
эксп.	1.505	1.46	1.46	1.41 Å

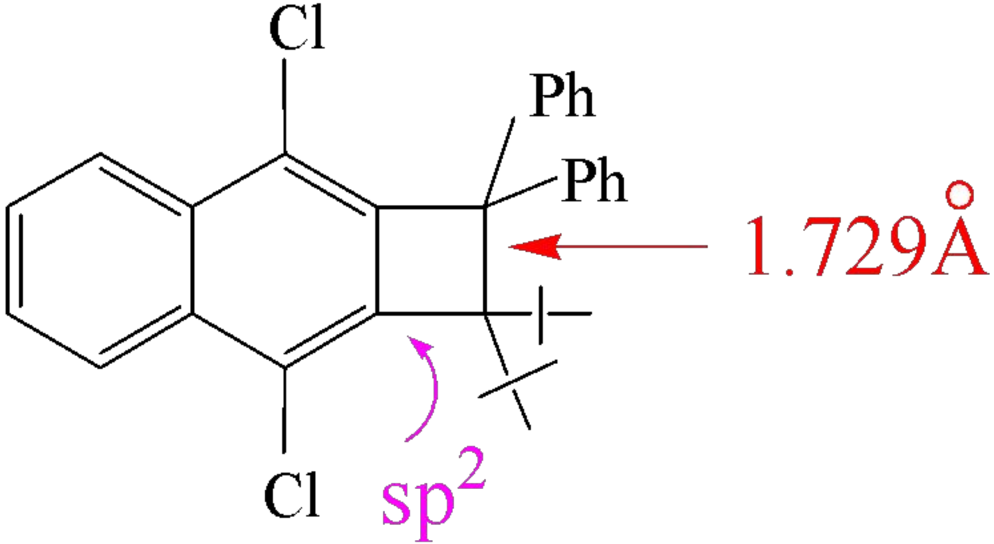
Необычно длинные связи



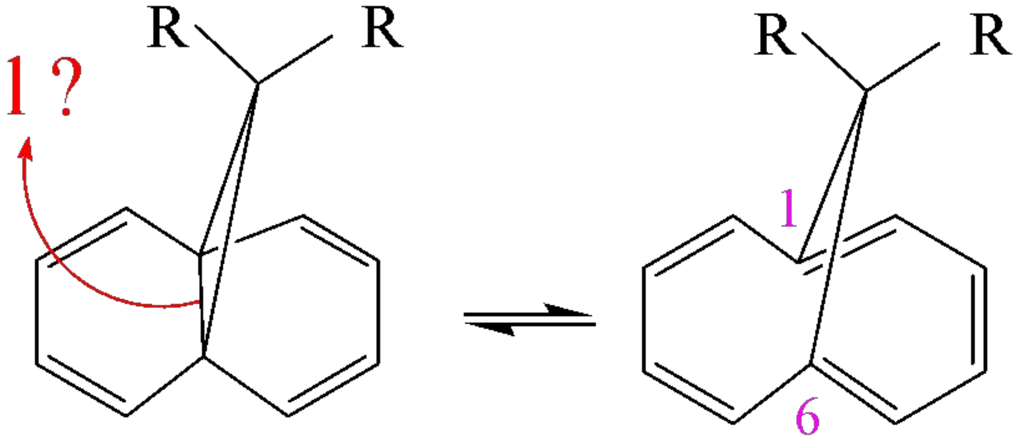


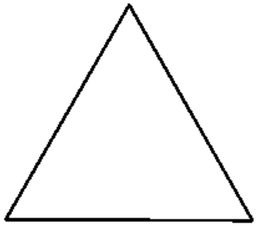


ЖСХ **1984**, 142



J. Org. Chem., **1999**, 3102





1.570 Å

R = CN **l** = 1.543 Å

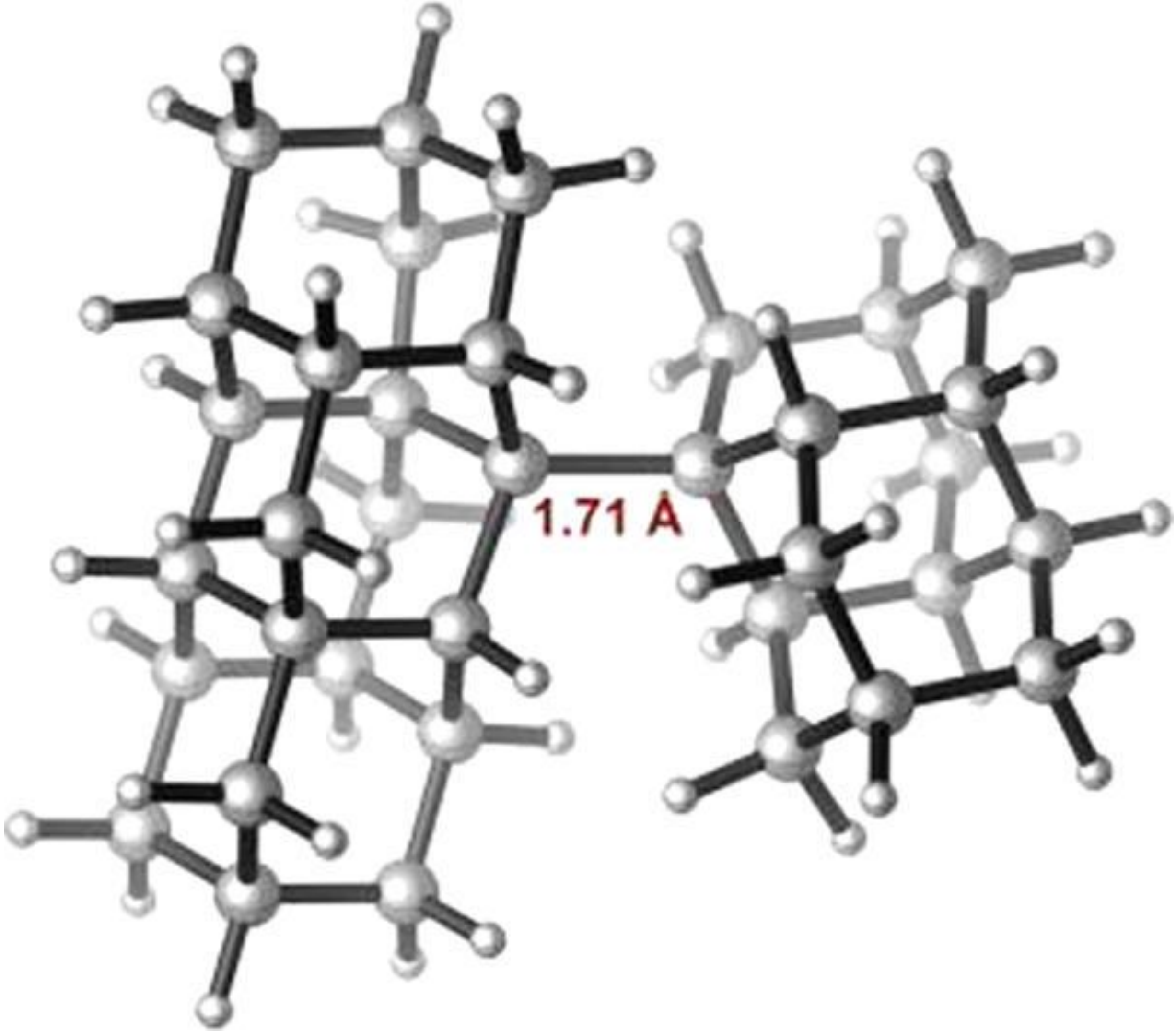
R = Me **l** = 1.770 Å lim

R = F **l** = 2.269 Å

Высокая эллиптичность связи C^1-C^6

Атомы в молекулах. Р. Бейдер. 2001.

2-(1-diamantyl)[121]tetramantane



J. Am. Chem. Soc. 2012, 13641

Энергия «искажения»

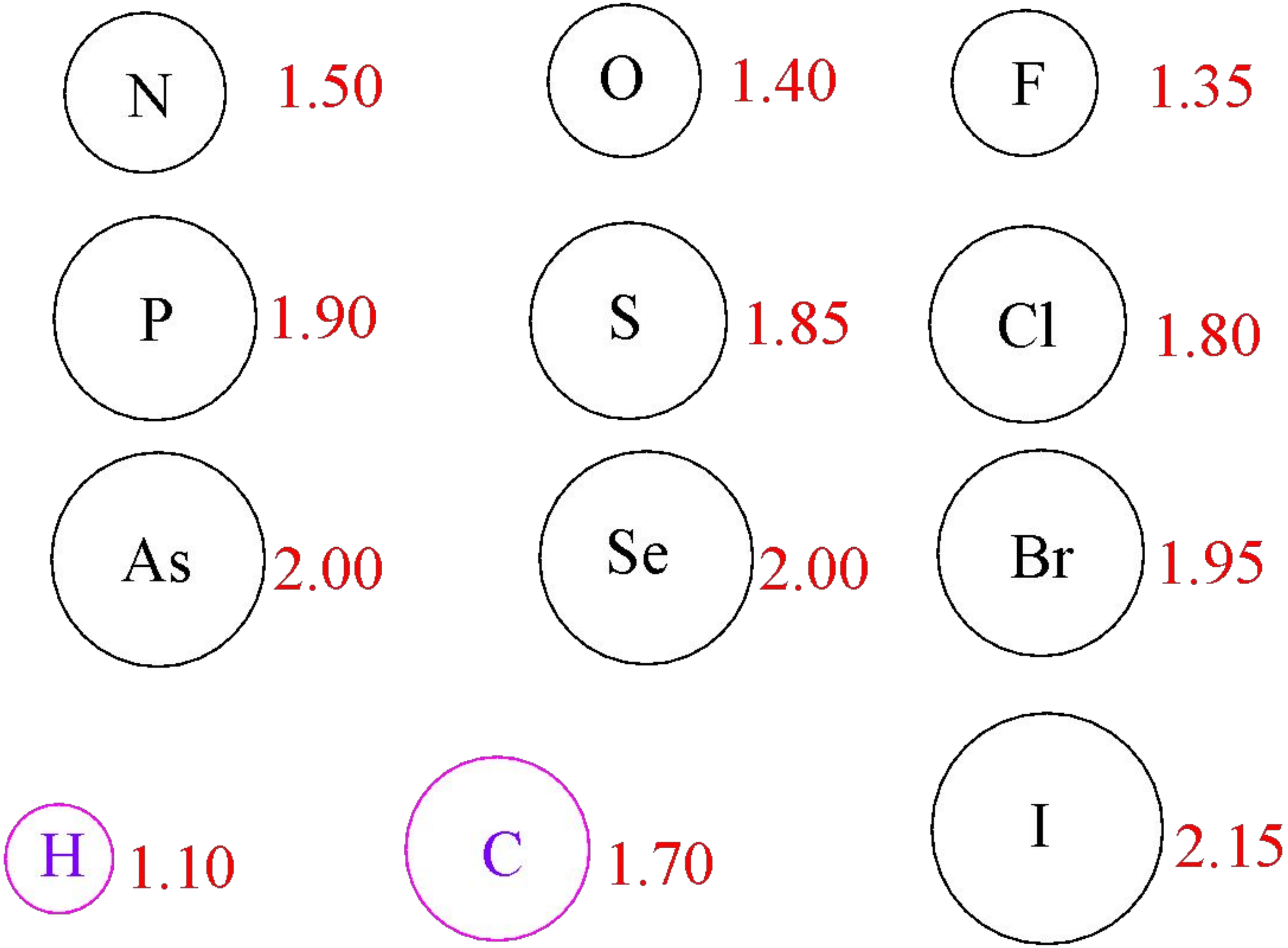
Удлинение связи:

$$E_l = \Sigma k_l (\Delta l)^2$$

Деформация углов:

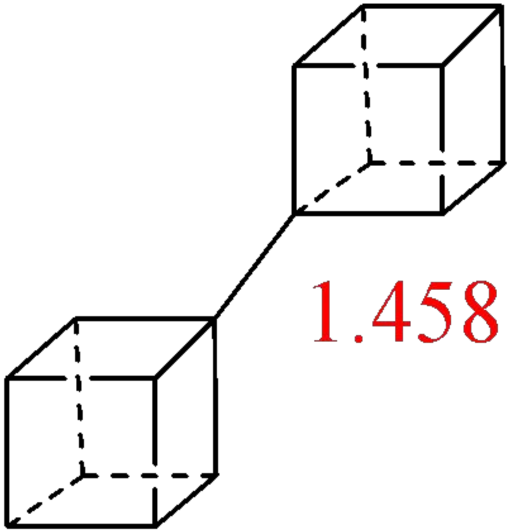
$$E_\varphi = \Sigma k_\varphi /2 (\Delta\varphi)^2$$

Ван-дер-ваальсовсы радиусы

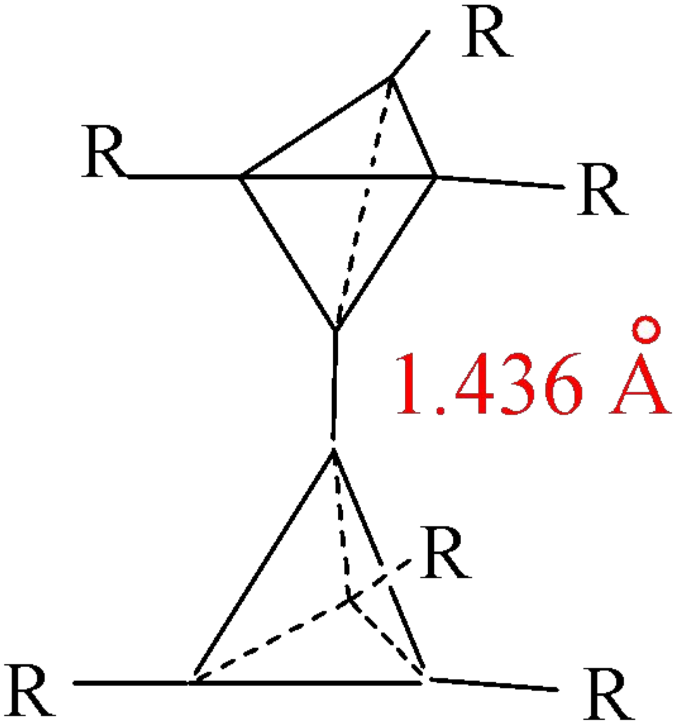


Л. Полинг, П. Полинг. Химия. М.: Мир, 1978; R. S. Rowland and R. Taylor, J. Phys. Chem., 100, 7384(1996); A. Bondi, J. Phys. Chem., 68, 441 (1964)

«Сжатие» C-C связи



1.458 Å



1.436 Å

R = $SiMe_3$

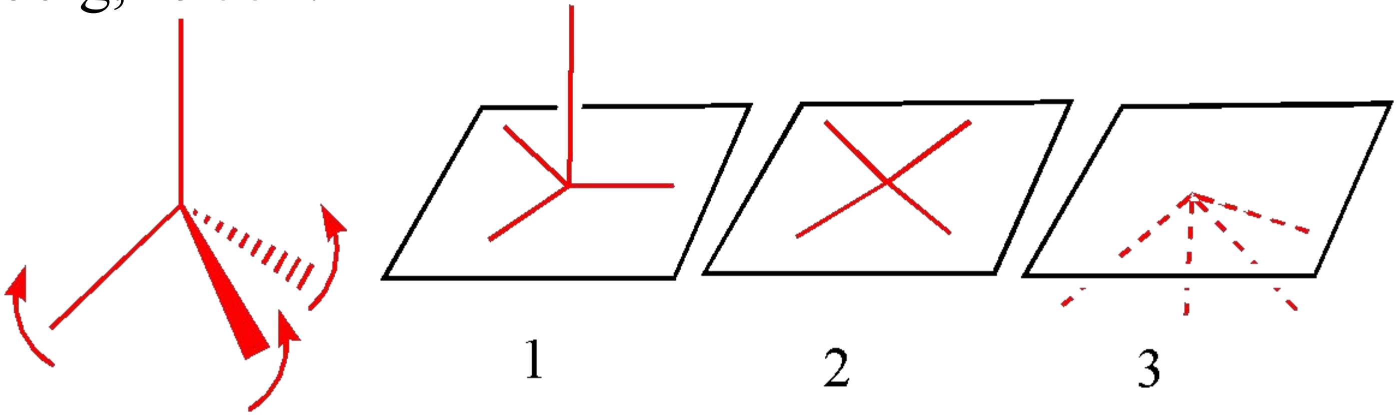
$H_3C\text{—}CH_3$

1.540 Å

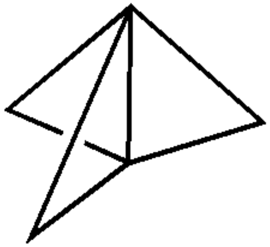
Ang. Chem. Int., **2005**, 5821

Соединения с инвертированной тетрагональной геометрией

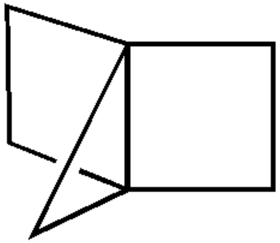
K. Wiberg, 1968 г.



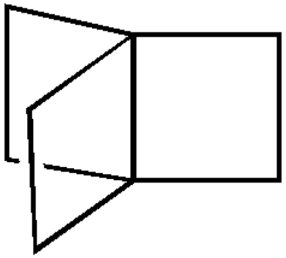
Пропелланы



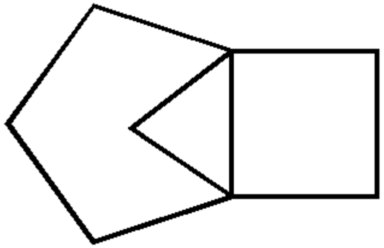
1,1,1-



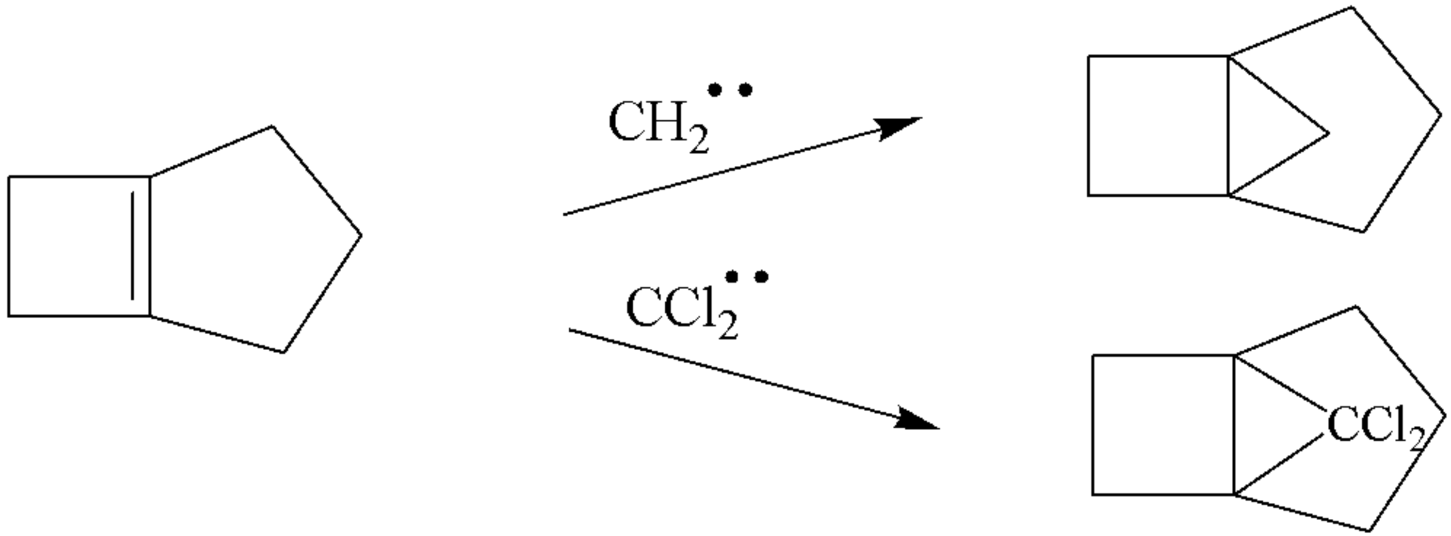
1,2,2-

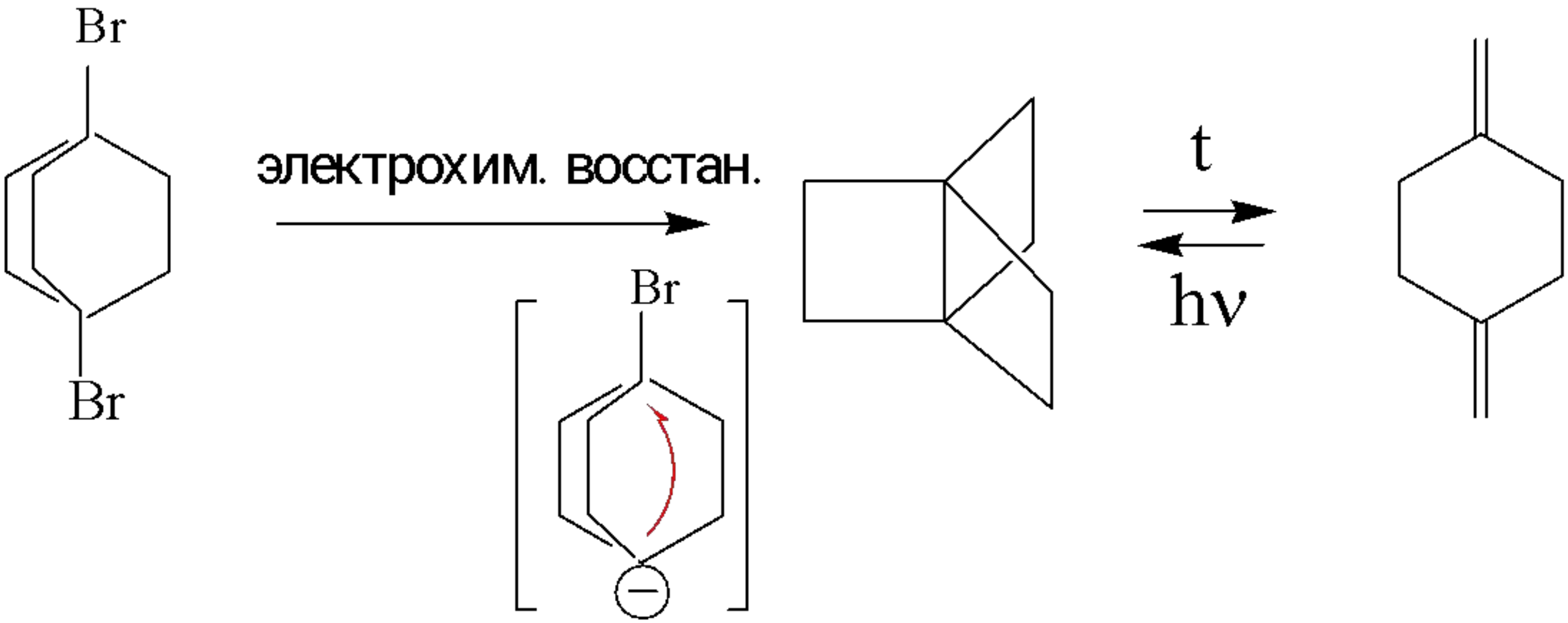


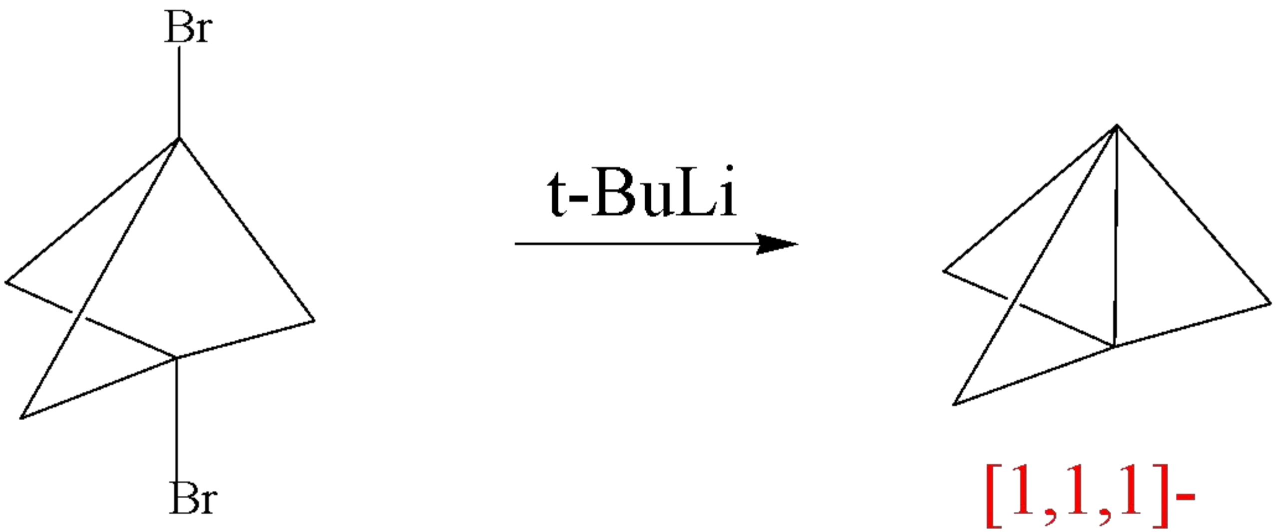
2,2,2-



1,2,3-

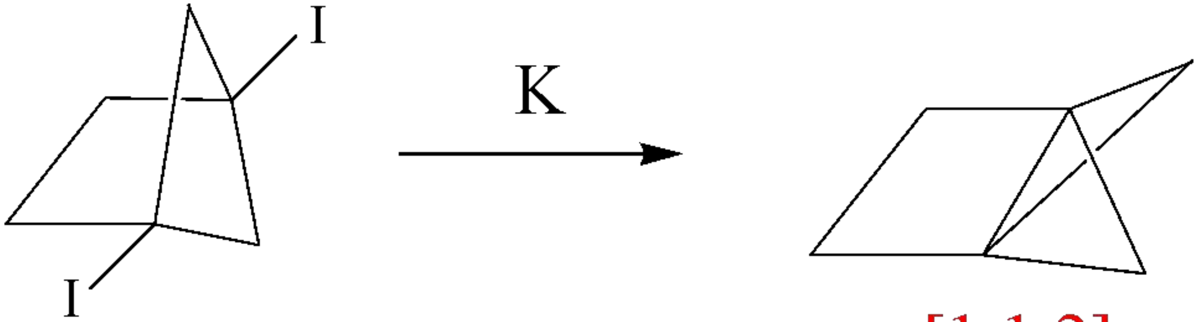

CH₂
CCl₂
CCl₂


Br
Br
электрохим. восстан.
Br
t
hν



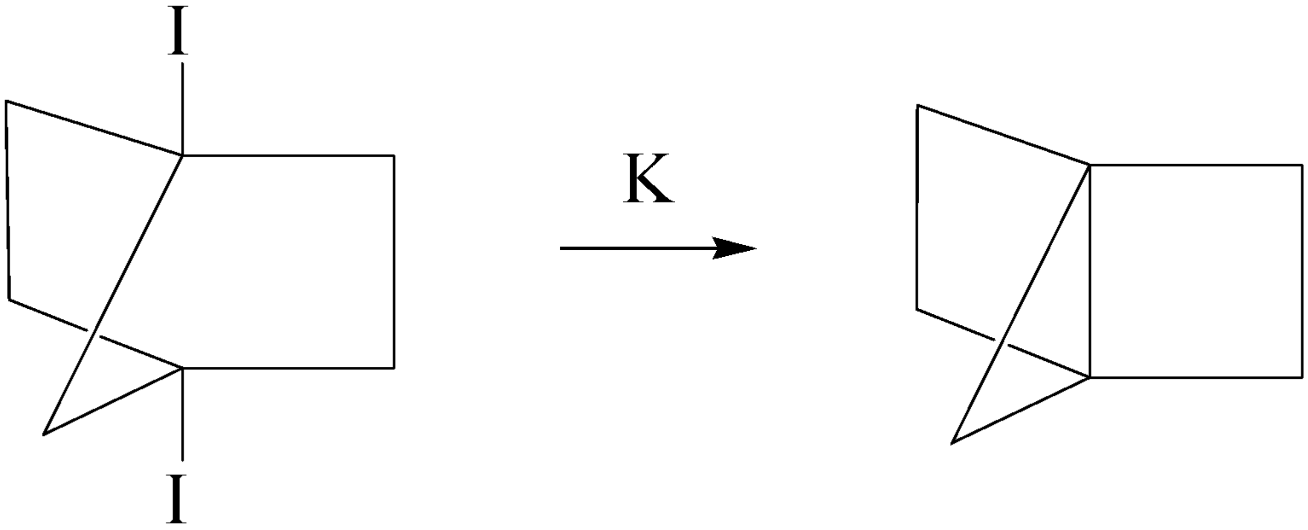
[1,1,1]-

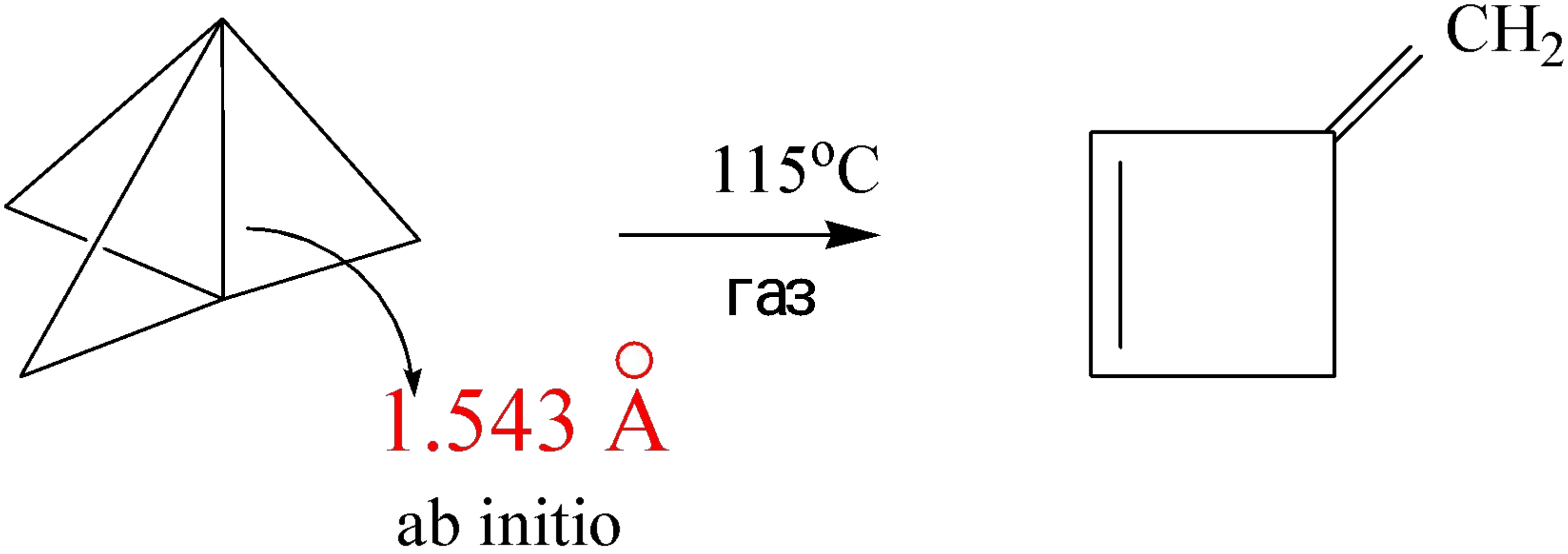
ЯМР ^{1}H: δ, м.д., 2.06 ЯМР ^{13}C: δ, м.д., 1.0 (C), 74.2 (CH_2)



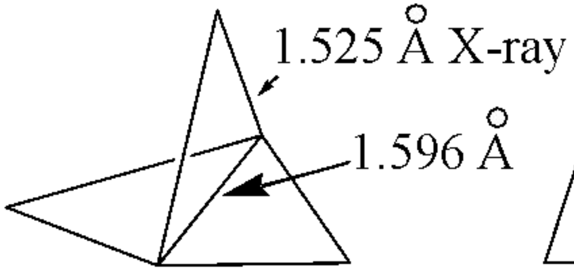
[1,1,2]-

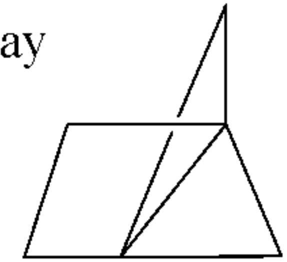
K. Wiberg et al., JACS **1982**, 5239; **1983**, 3635

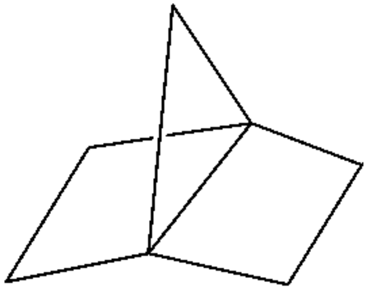

I
I
K


1.543 Å
ab initio
115°C
газ
CH2

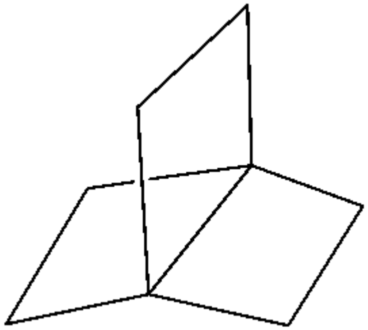
Энергия напряжения SE

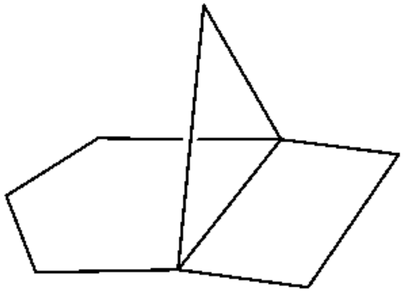






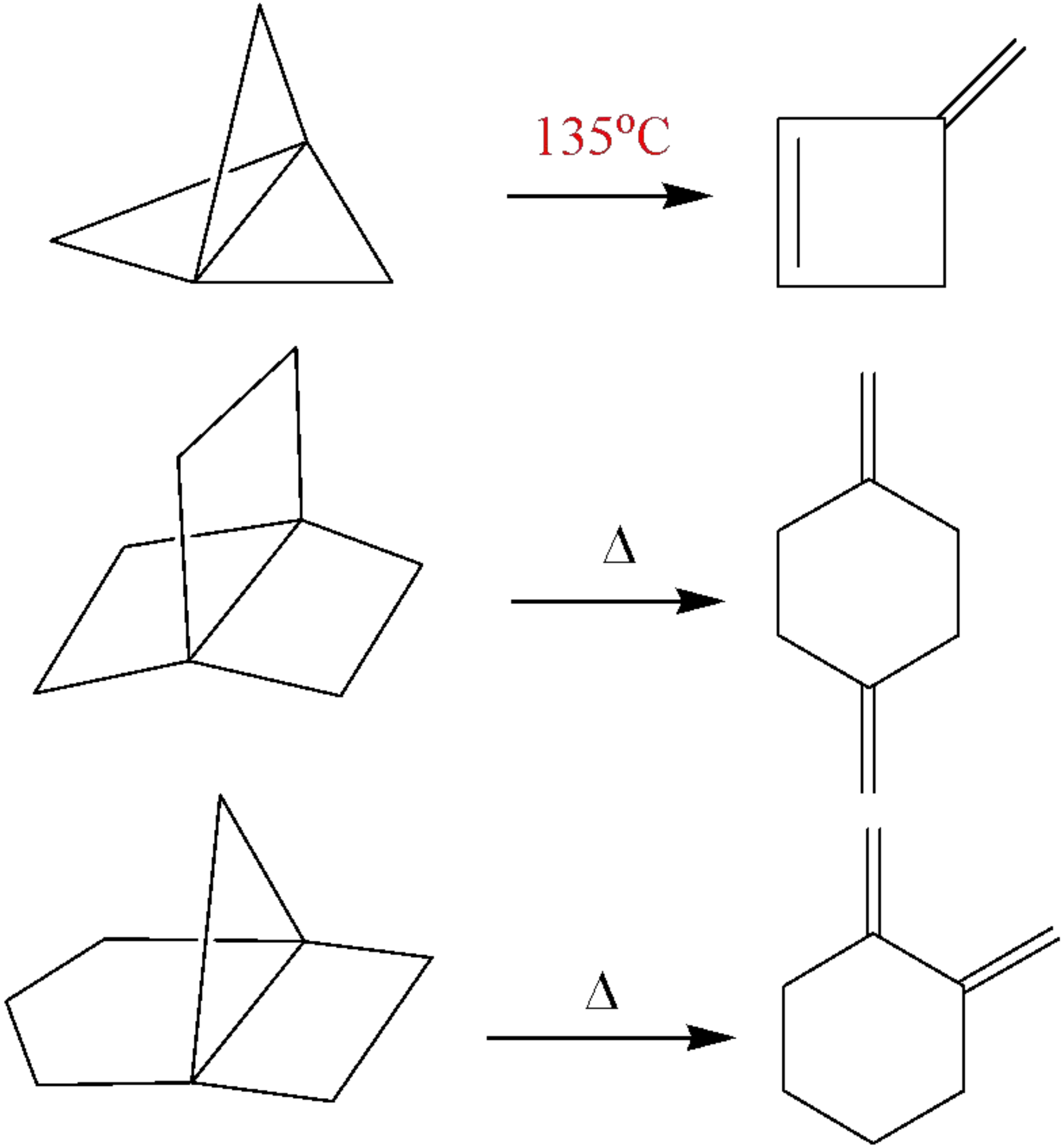
SE, ккал/моль	102	104	102





SE, ккал/моль	93	67	ab initio 6-31G

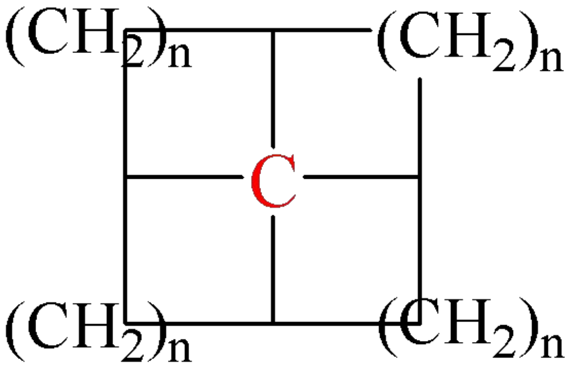
Acc. Chem. Res. **1984**, 379



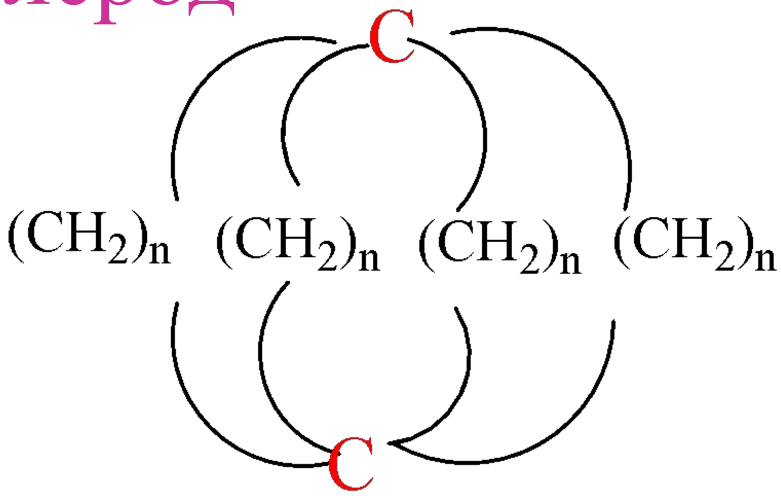
$t_{1/2}$ 1 час, 20°C

$t_{1/2}$ 1 час, 320°C

Планарный углерод



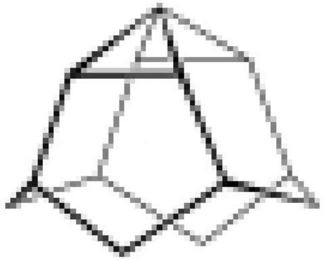
фенестраны



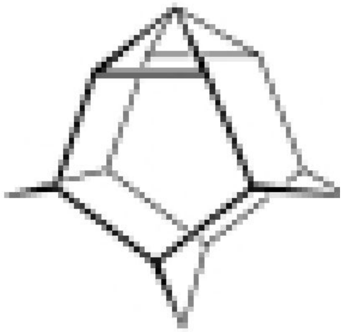
пэддланы

IV

5

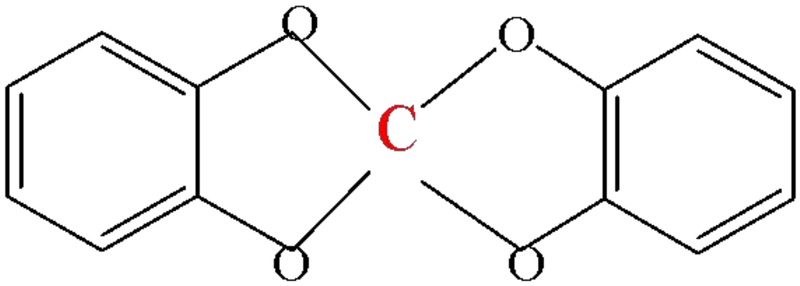


6

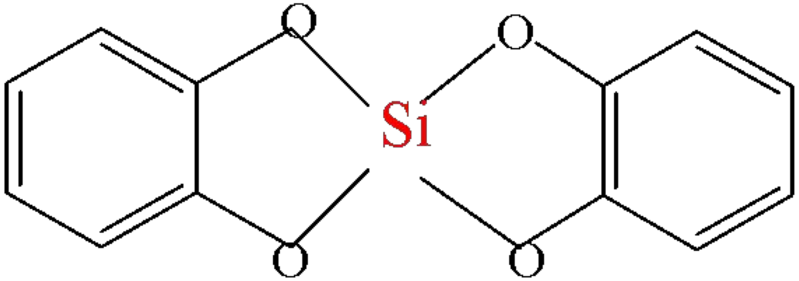


7

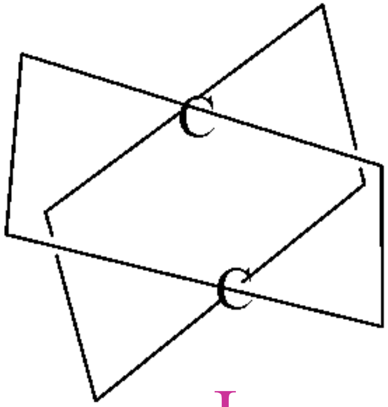
В кристалле



II (тетраэдр)



III (планарен)



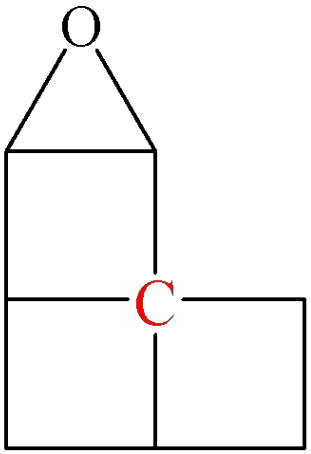
I

ab initio (STO-3G)
ΔΔE, ккал/моль

CH_4	240
SiH_4	152

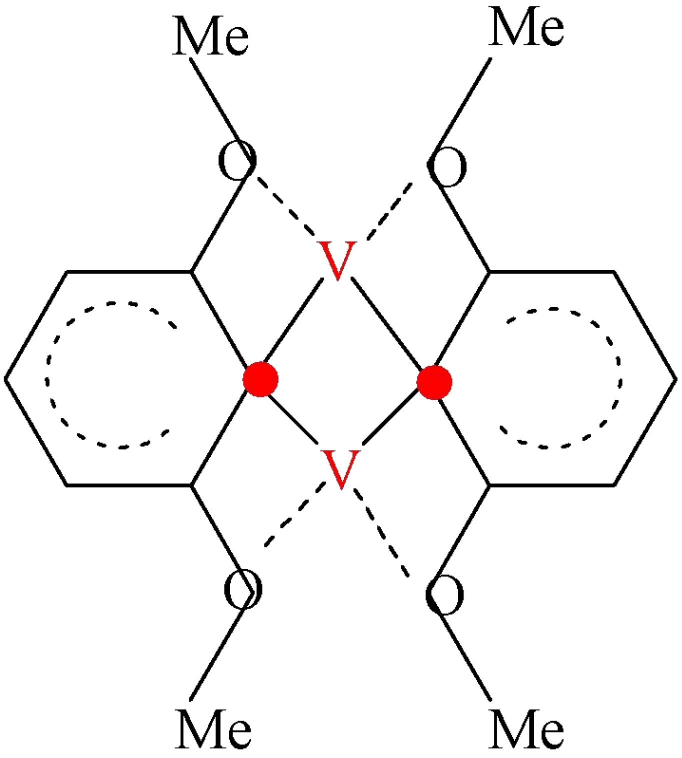
Редакция J. Chem. Res. (1977 г.)

«Первый синтез производного планарного тетракоординированного С»



страсбурген

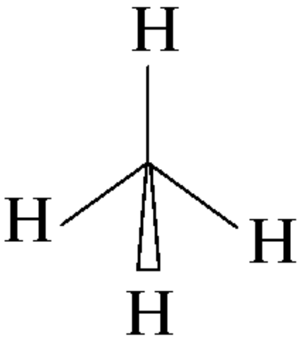
Рислинг, 1977 г.

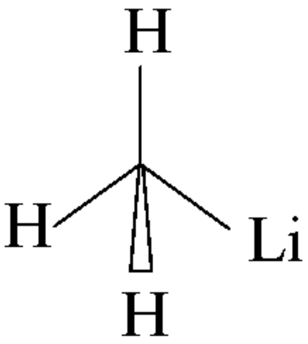


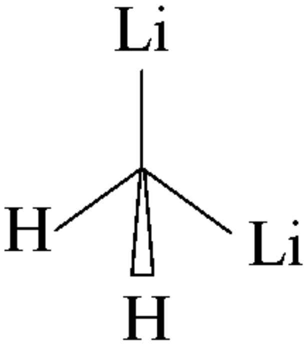
Cotton, Millar, JACS, 1977

«Планаризация» соединений углерода

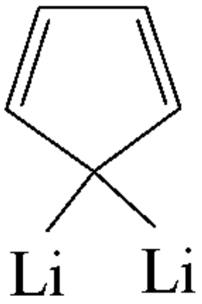
ab initio

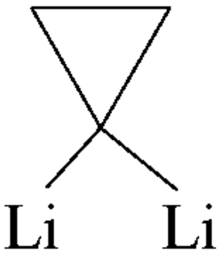






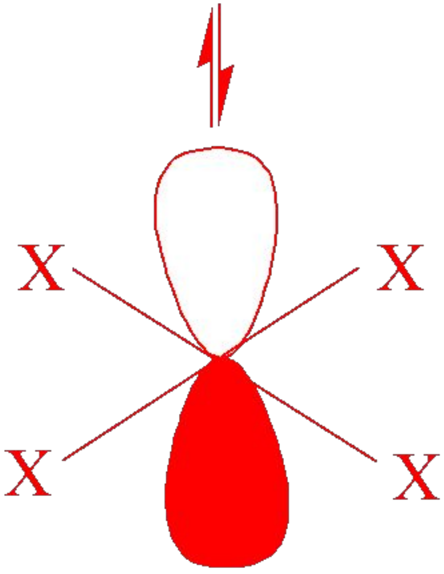
ΔΔE, ккал/ моль 122 52 17



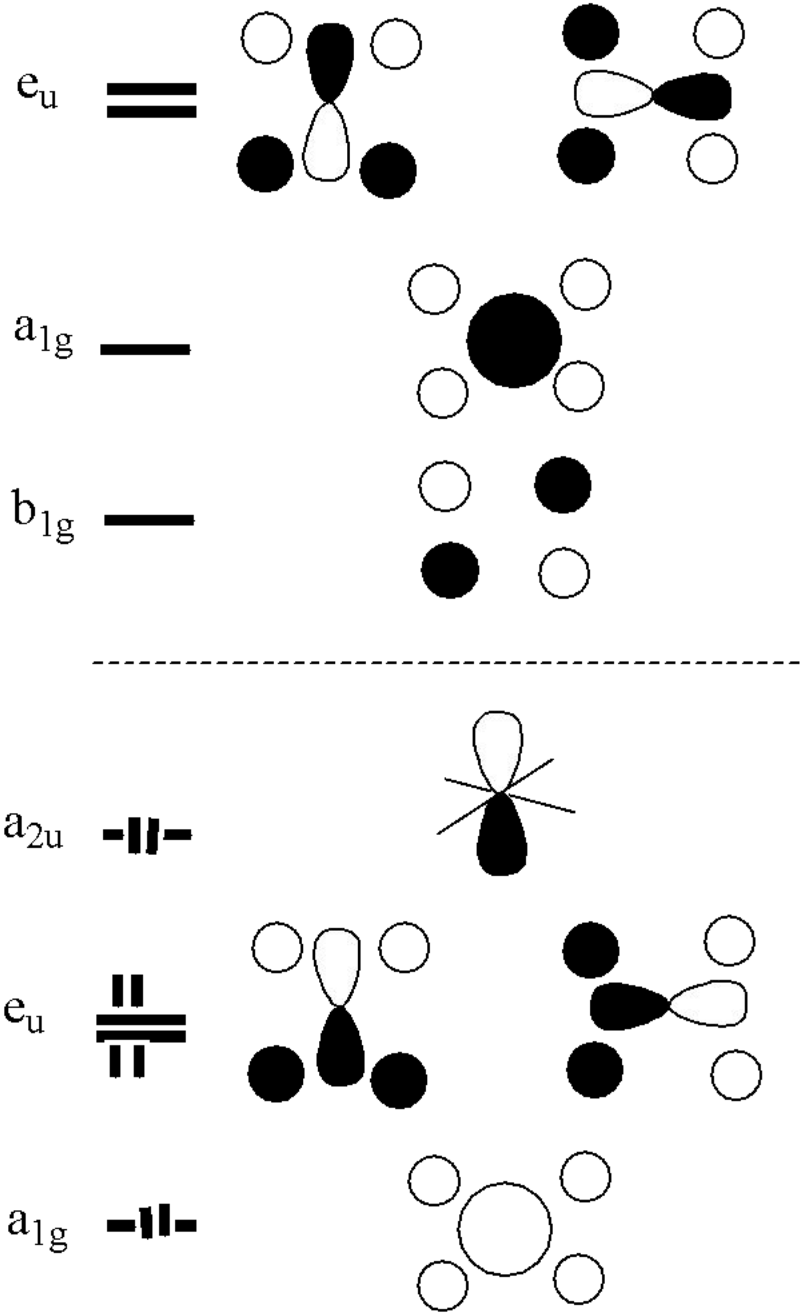


ΔΔE, ккал/ моль 16 -7

P. Schleyer et al. Ang. Chem. Int., **1997**, 815

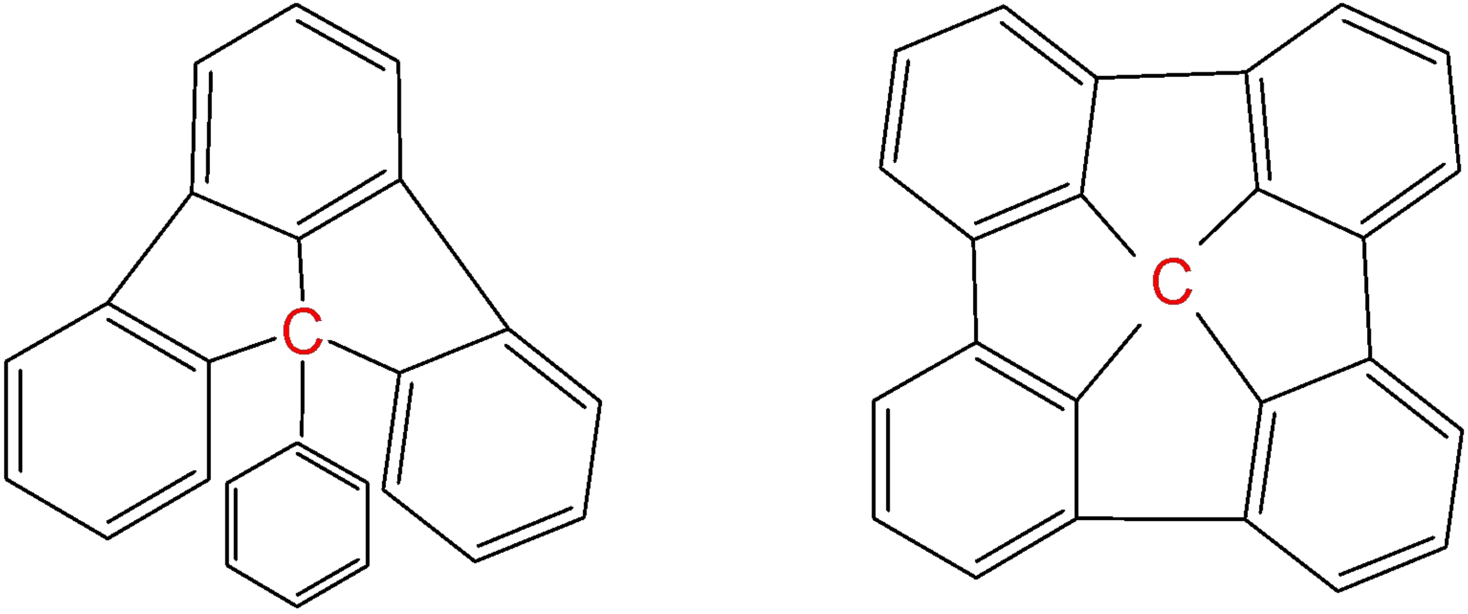


a_{2u}



Fluradenes

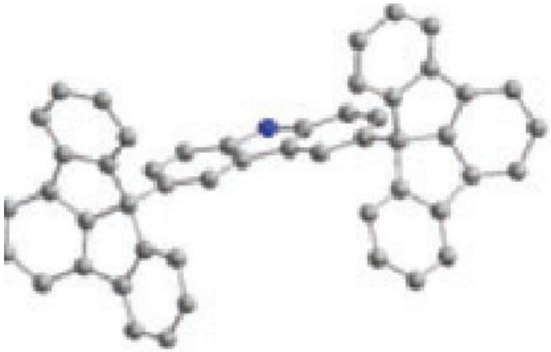
Q. Liu et al., Chem. Comm. **2011**, 2155



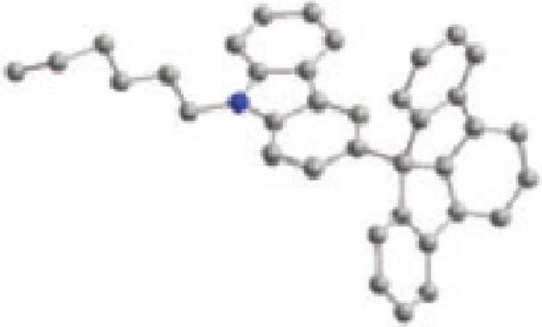
Не синтезированы

Fluradenes

Q. Liu et al., Chem. Comm. **2011**, 2155



4a



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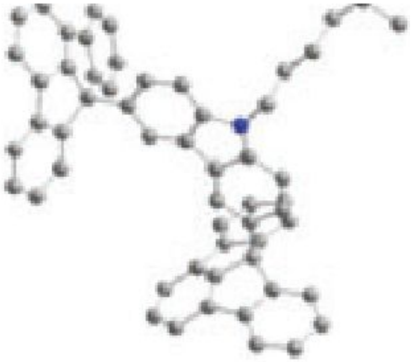

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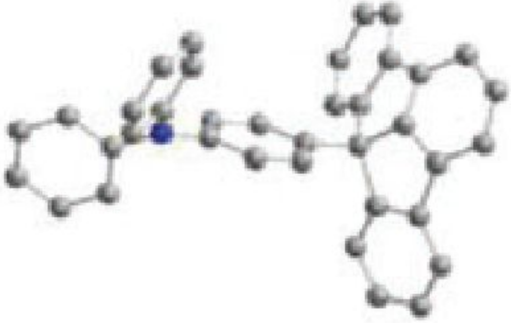

4ca

4cb