

Strukturaufklärung in der molekularen anorganischen Chemie

1. Einführung

Molekülstruktur, Geschichte

„Bernhard von Chartres sagte, wir seien gleichsam Zwerge, die auf den Schultern von Riesen sitzen, um mehr und Entfernteres als diese sehen zu können – freilich nicht dank eigener scharfer Sehkraft oder Körpergröße, sondern weil die Größe der Riesen uns emporhebt.“

– Johannes von Salisbury: *Metalogicon* (1159) 3, 4, 47–50

Molekülstruktur, Butlerow

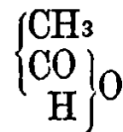


Alexander Michailowitsch Butlerow

1864:

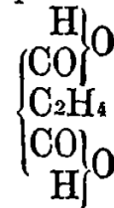
Въ самомъ дѣлѣ, сравнивая рациональныя формулы уксусной и янтарной кислотъ легко замѣтить, что роли радикала мѣфила (въ кислотѣ уксусной) и эфилена (въ кислотѣ янтарной)—аналогичны:

• уксусная кислота



Essigsäure

янтарная кислота



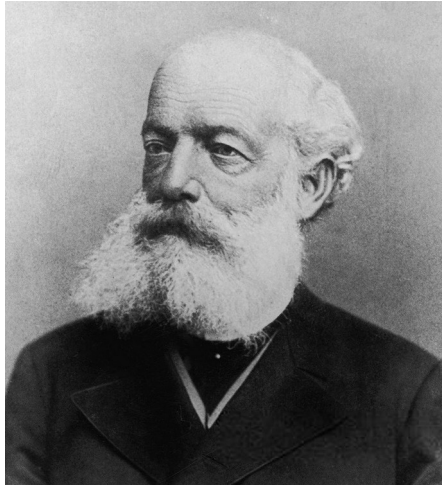
Bernsteinsäure



Alexander Michailowitsch Butlerow

1828 – 1886

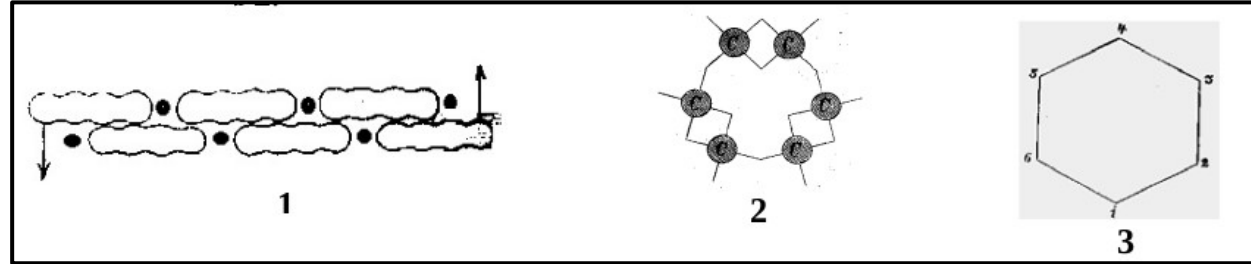
Molekülstruktur, Kekulé



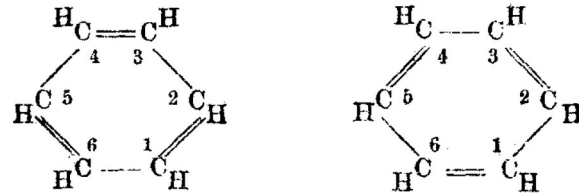
August Kekulé

1829 – 1896

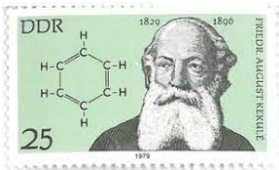
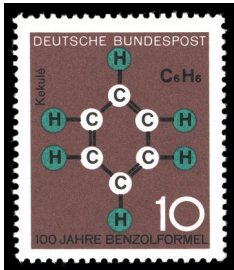
C_6H_6 1859 – 1863:



1865:

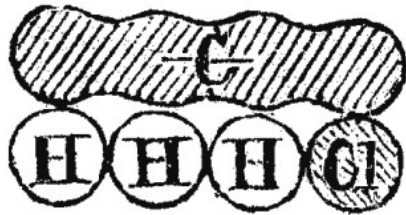


Aug. Kekulé, "Sur la constitution des substances aromatiques", *Bulletin de la Société Chimique de Paris*, 1865, 3 (2), 98–110.

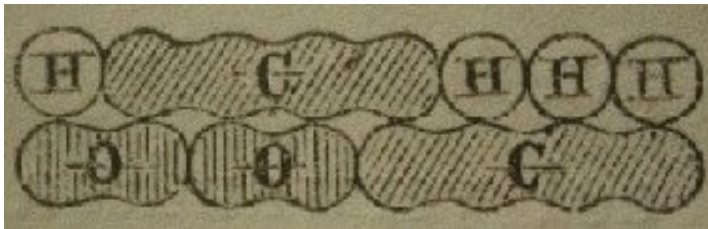


Molekülstruktur, Kekulé

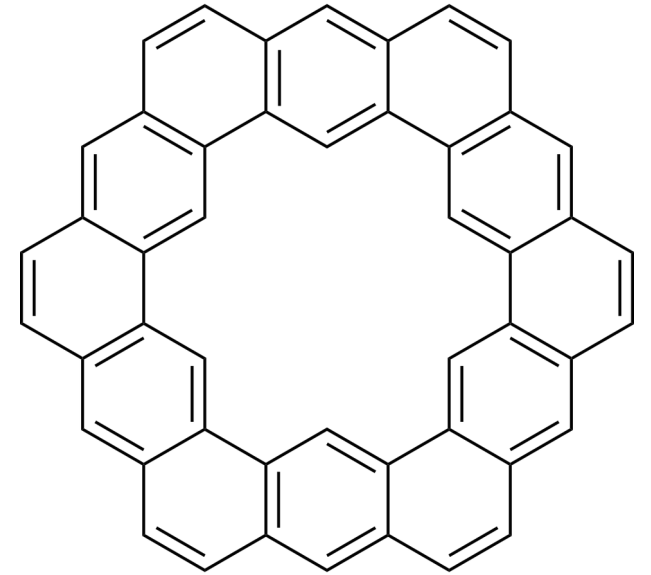
CH₃Cl, 1866:



Essigsäure, 1866:

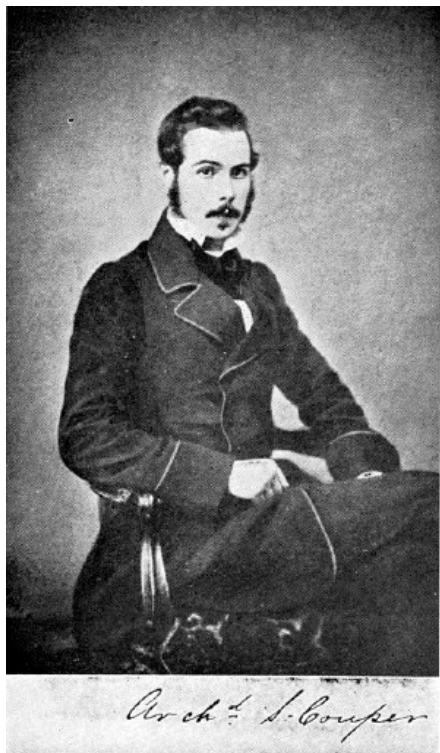


Kekulen, 1978:



F. Diederich, H. A. Staab, „Benzenoid versus Annulenoid Aromaticity: Synthesis and Properties of Kekulene“, *Angew. Chem. Int. Ed.* 1978, 17 (5), 372–374.

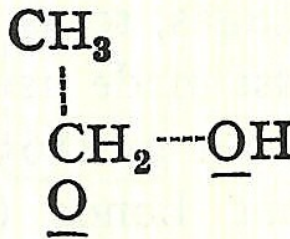
Molekülstruktur, Couper



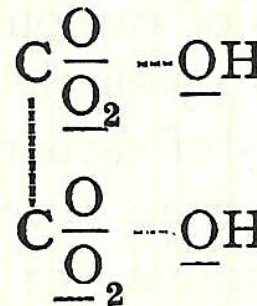
Archibald Scott Couper

1831 – 1892

"Neue chemische Theorie" 1858:

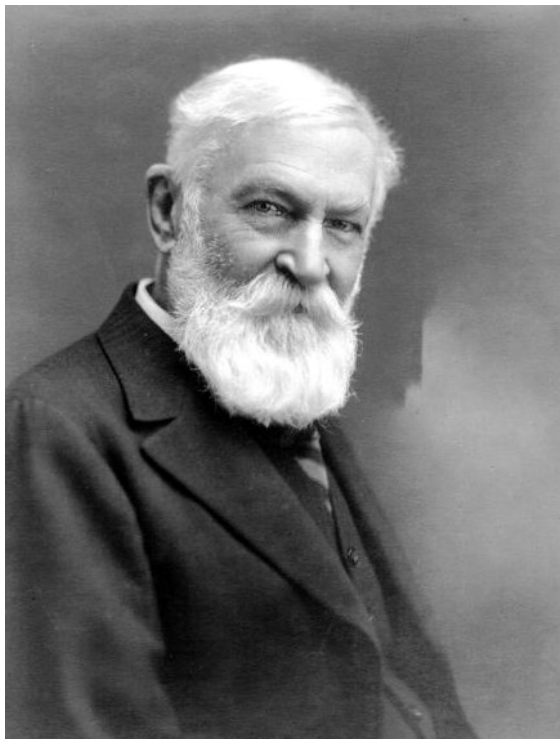


Ethanol



Oxalsäure

Molekülstruktur, Crum Brown

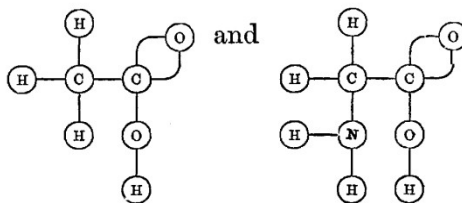


Alexander Crum Brown

1838 – 1922

Essigsäure

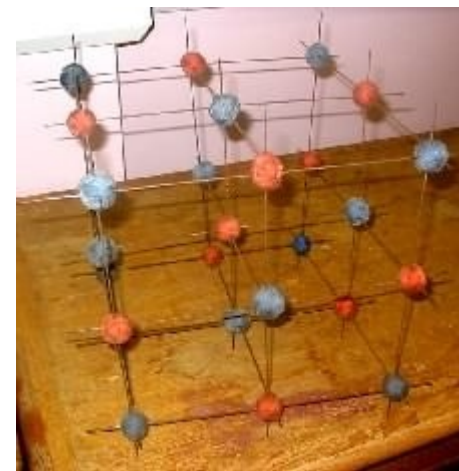
Glycin



We here see the hydrogen and the ammonia residue NH₂ exerting a “disturbing” influence on the relation of oxygen to hydrogen through two carbon-atoms. Many other examples will at once

* Butlerow notices this disturbing influence (Zeitschrift, vi. 516) as opposing an obstacle, which he seems to regard as for the present insuperable, in the way of determining whether a difference exists or not among the equivalents of a multivalent atom.

NaCl Kristall:



A. C. Brown, „On the Theory of Isomeric Compounds“, *J. Chem. Soc.*, 1865, 18, 230–245.

X-Rays



Wilhelm Conrad Röntgen
1838 – 1922

1895: X-Rays



Max von Laue
1879 – 1960

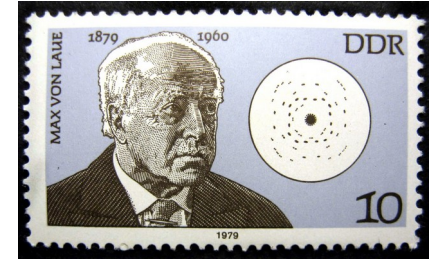
1914: Nobelpreis für Physik



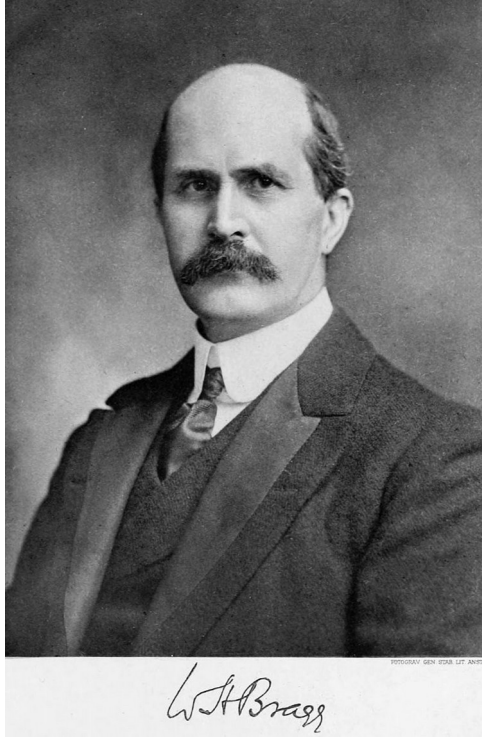
Die Relativitätstheorie

Korpuskular- und Wellentheorie

Die Interferenzen von Röntgen- und
Elektronenstrahlen

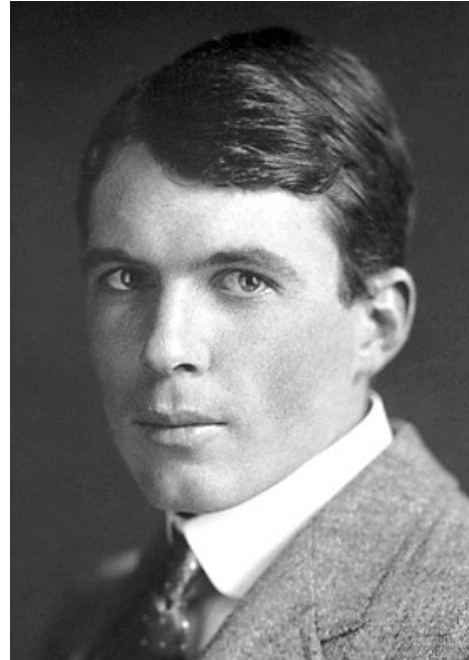


Kristallstruktur, Braggs



William Henry Bragg

1862 – 1942



William Lawrence Bragg

1890 – 1971



1915: Nobelpreis für Physik „für ihre Verdienste um die Erforschung der Kristallstrukturen mittels Röntgenspektroskopie“

Molekülstruktur, Odd Hassel



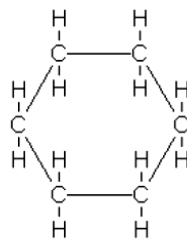
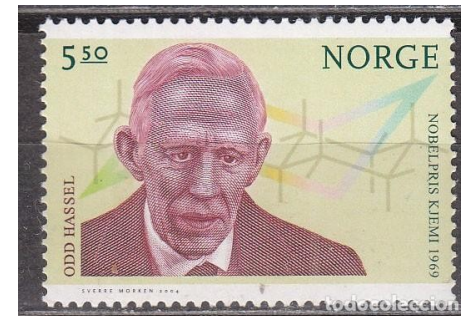
Odd Hassel

1897 – 1981

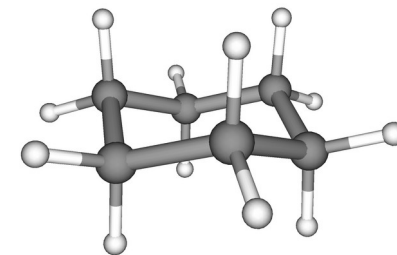
Gas-Elektronenbeugung

Sesselstruktur des Cyclohexans

1969: Nobelpreis für Chemie



2D



3D

Molekülstruktur/GED, Lev Vilkov



Lev Vasilievich Vilkov in Lomonossow-Universität Moskau

1931 – 2010

Gas-Elektronenbeugung: Entwicklung von A bis Z

Inwiefern sind verfeinerte Molekularparameter experimentell?

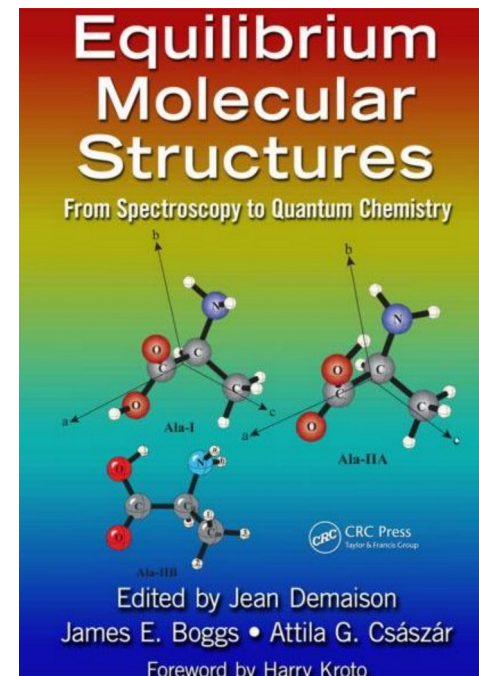
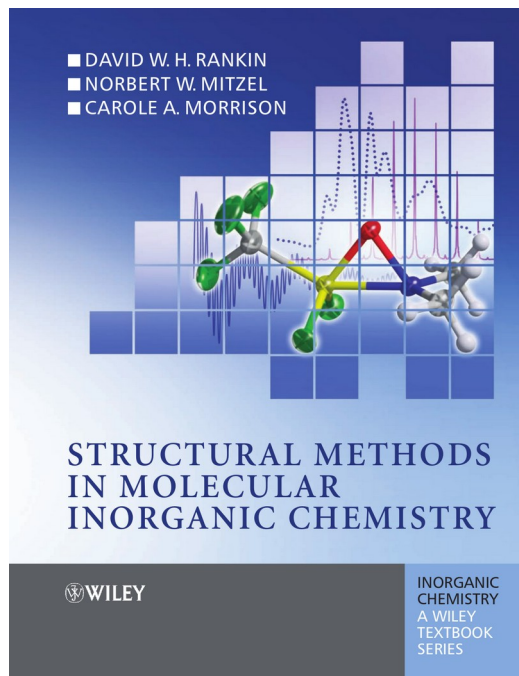
Strukturchemie: 6 Bücher, 27 Reviews, über 300 Papers, ...

Lehre: ~30 Doktorarbeiten, 6 Habilitanden

Strukturmethode

aktueller Stand

Molekülstruktur, Bücher

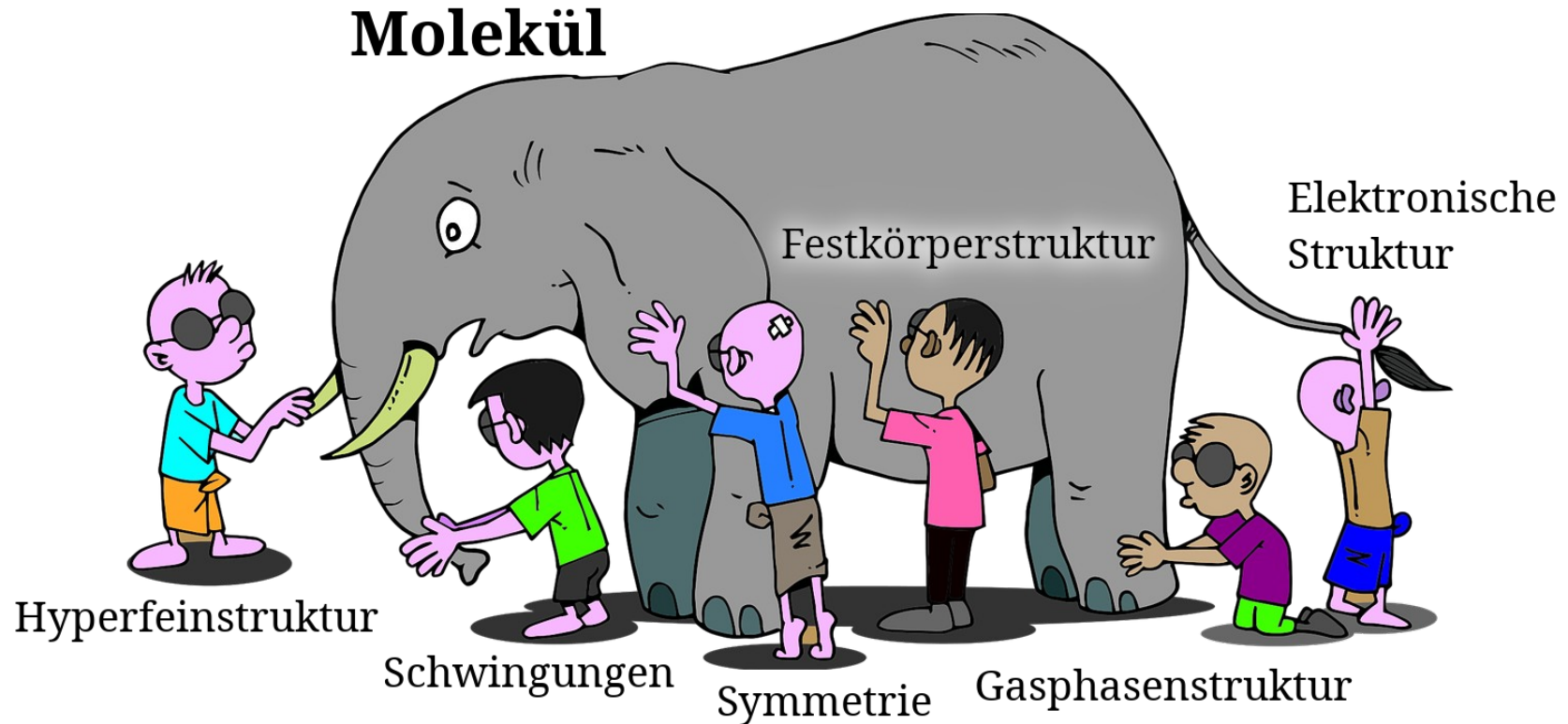


D. W. H. Rankin, N. W. Mitzel, C. A. Morrison, Structural Methods in Molecular Inorganic Chemistry, John Wiley & Sons, Chichester, 2013.

M. Reichenbacher, J. Popp, Challenges in Molecular Structure Determination, Springer, New York, 2012.

J. Demaison, J. E. Boggs, A. G. Csaszar, Eds., Equilibrium Molecular Structures: From Spectroscopy to Quantum Chemistry, CRC Press, Boca Raton, 2010.

Struktur?



Born-Oppenheimer-Näherung

Wiki (de):

$$\hat{H}_{\text{mol}} \cdot \Psi_{\text{mol}}(\vec{r}, \vec{R}) = E \cdot \Psi_{\text{mol}}(\vec{r}, \vec{R})$$

$$\hat{H}_{\text{mol}} = \hat{T}_e + \hat{T}_N + \hat{V}_{ee} + \hat{V}_{NN} + \hat{V}_{eN}$$

$$\hat{T}_e = -\sum_{i=1}^n \frac{\hbar^2}{2m_e} \nabla_i^2$$

$$\hat{T}_N = -\sum_{I=1}^N \frac{\hbar^2}{2M_I} \nabla_I^2$$

$$\hat{V}_{ee} = \frac{q_0}{4\pi\epsilon_0} \sum_{i<j} \frac{1}{|\vec{r}_i - \vec{r}_j|}$$

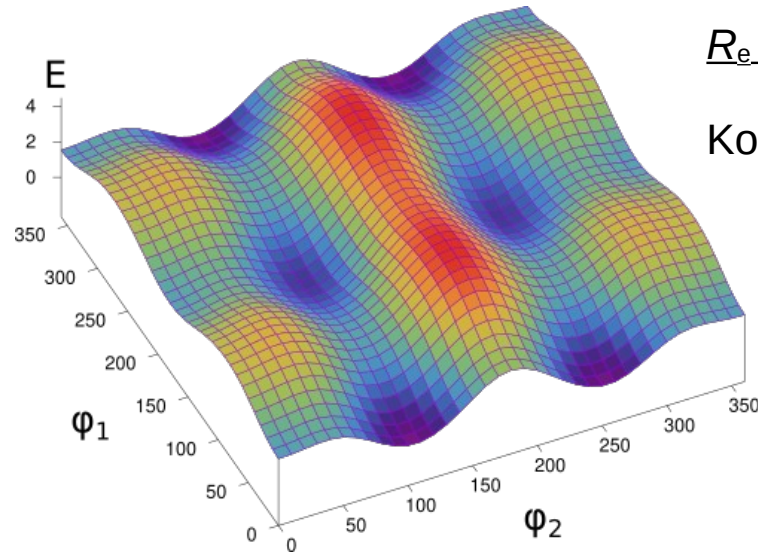
$$\hat{V}_{NN} = \frac{q_0}{4\pi\epsilon_0} \sum_{I<J} \frac{Z_I Z_J}{|\vec{R}_I - \vec{R}_J|}$$

$$\hat{V}_{eN} = -\frac{q_0}{4\pi\epsilon_0} \sum_{i,I} \frac{Z_I}{|\vec{r}_i - \vec{R}_I|}$$

$$\Psi_{\text{mol}} = \phi \cdot \eta$$

$$\phi = \phi(\vec{r}, \vec{R})$$

$$\eta = \eta(\vec{R})$$



Achtung! Fehler in wiki (mind. Okt. 2022):

$$\hat{H}_e \cdot \phi_h(\vec{r}, \vec{R}) = E_h(\vec{R}) \cdot \phi_h(\vec{r}, \vec{R})$$

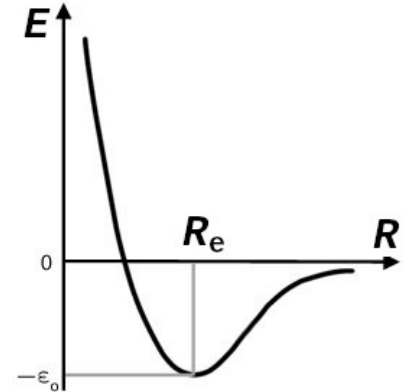
$$\hat{H}_e = \hat{T}_e + \hat{V}_{ee} + \hat{V}_{eN}$$

$$(\hat{T}_n + \hat{V}_{NN} + E_h(\vec{R})) \cdot \eta_{hk}(\vec{R}) = E_{hk} \cdot \eta_{hk}(\vec{R})$$

$E_h(R)$ – adiabatische Energie

R_e – Gleichgewichtsstruktur

Konformer \neq Konformation !



Klassifizierungen der Methoden

Wechselwirkung mit Strahlung:

- (Optische/Radio) Spektroskopie
- Diffraktion
- Elektrische Methoden
- Ionisation

Probe Beeinflussung:

- Destruktiv
- Nicht destruktiv

Anwendung:

- Identifizierung/Sauberkeit
- Elementaranalyse
- Chemische Gruppen
- Chemische Konnektivität
- Konformations-Eigenschaften
- Symmetrie
- Geometrie (Längen, Winkel)
- Schwingungen
- Elektronische Struktur (Dichte)
- (Elektrische) Dipolmomente

Charakteristische Zeit:

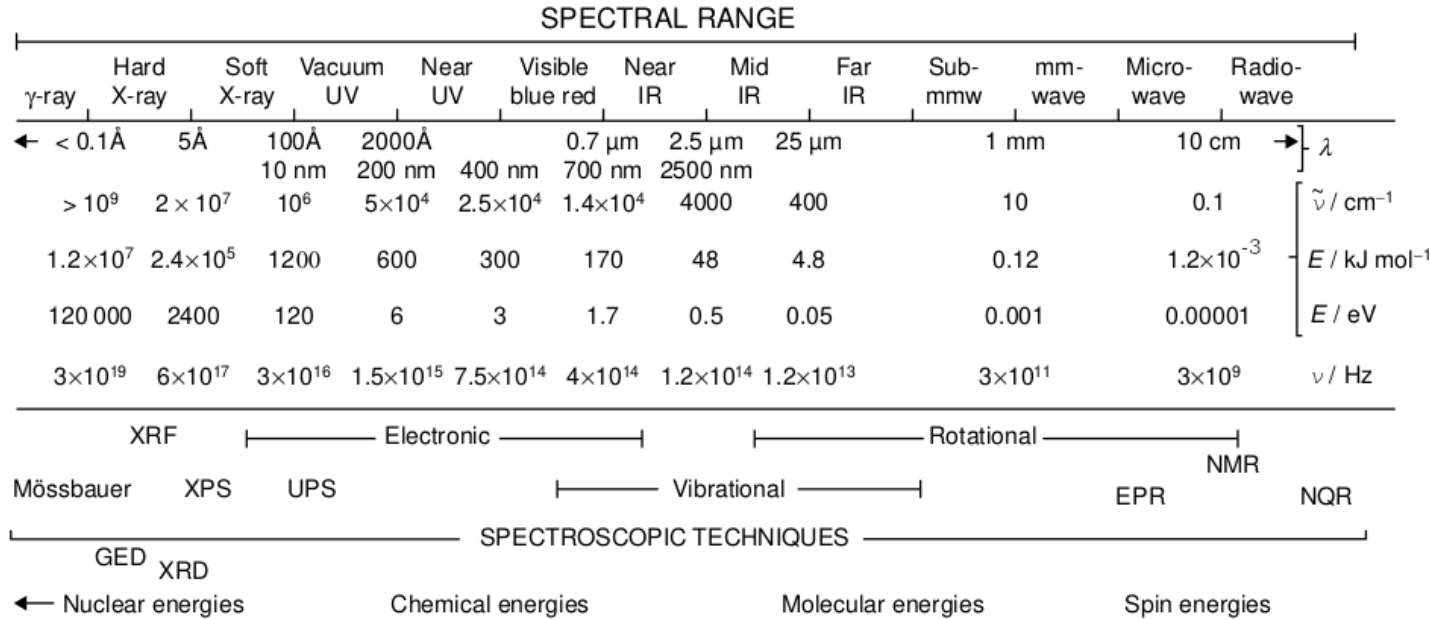
- Langsame Methoden
- Schnelle Methoden

Aggregatzustand der Probe:

- Gas
- Flüssigkeit
- Feststoff

Spektroskopie \neq Spektrometrie !

Das Energiespektrum



$$\tilde{\nu} = \frac{\nu}{c} = \frac{1}{\lambda} = \frac{N}{l}$$

$$E = h\nu$$

λ – Wellenlänge

ν – Frequenz

c – Phasengeschwindigkeit

E – Energie

h – Planck-Konstante

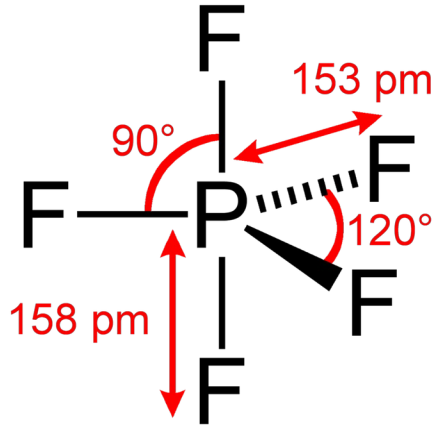
ν̃ – Wellenzahl (Quotient aus der Anzahl N der auf die Länge l entfallenden Wellenlängen)

Charakteristische Zeit

Heisenbergsche Unschärferelation:

$$\Delta x \Delta p \geq \hbar/2$$

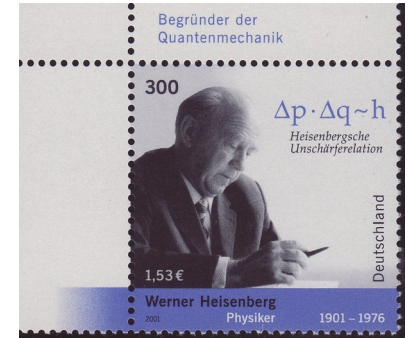
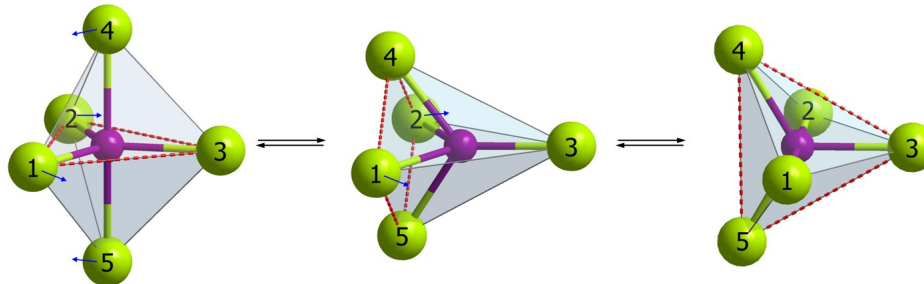
$$\Delta E \Delta t \geq \hbar$$



^{19}F NMR (langsam): $\delta(\text{F}_{\text{ax}}) = \delta(\text{F}_{\text{eq}})$ $r(\text{P-F}_{\text{ax}}) = r(\text{P-F}_{\text{eq}})$?

GED (sehr schnell): $r_g(\text{P-F}_{\text{ax}}) = 1.580(2) \neq r_g(\text{P-F}_{\text{eq}}) = 1.532(3) \text{ \AA}$

Berry-Pseudorotation:



Direktes vs. inverses Problem

$$Ax = u$$

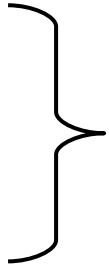
A – Operator (Modell)
 x – Parameter
 u – Daten



$$x = R(u)$$

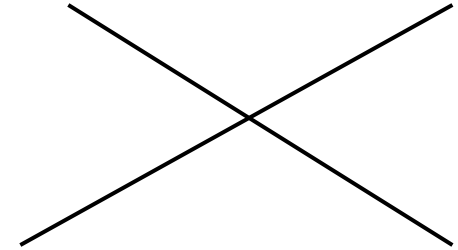
$$R = A^{-1}$$

Existenz
+
Eindeutigkeit
+
Stabilität



Gut gestelltes inv. Problem

$$y = xa_1 + b_1 \quad y = xa_2 + b_2$$



$$a_1 \neq a_2 \quad b_1 \neq b_2$$



$$a_1 \approx a_2 \quad b_1 \approx b_2$$

Themen in diesem Kurs

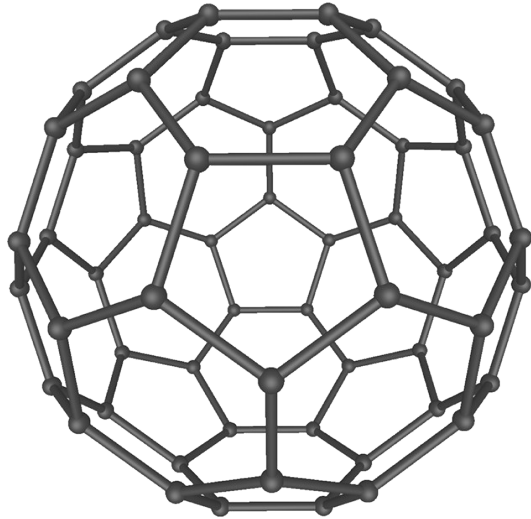
- Symmetrie
- Infrarotspektroskopie
- Raman-Spektroskopie
- Mikrowellenspektroskopie
- Rotations-Schwingungsspektroskopie
- Elektronische Struktur
- Diffraktion
- Gas-Elektronen-Diffraktion
- Diffraktion in kondensierter Materie
- Strukturverfeinerung, phasenabhängige Strukturen
- Kernresonanz-Spektroskopie
- Elektronenspinresonanz-Spektroskopie
- Massenspektrometrie

Molekül des Tages

Buckminsterfullerenen C_{60}

Anorganisches Molekül!

Symmetrie: I_h



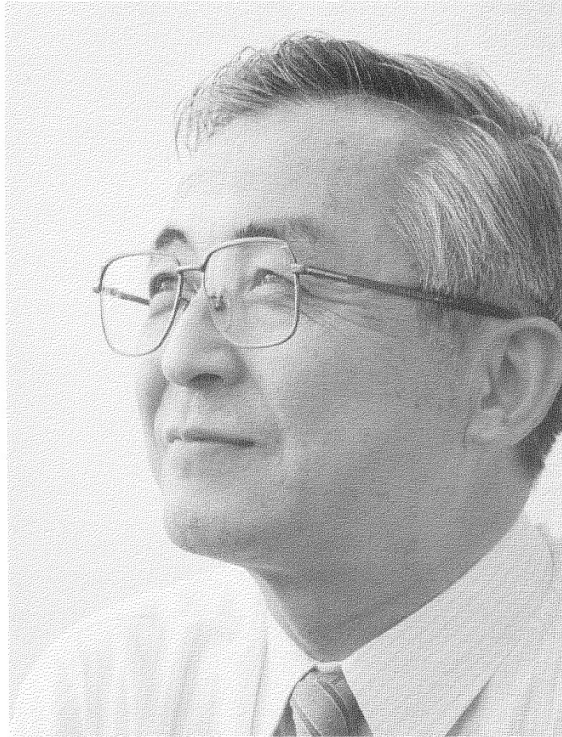
Richard Buckminster Fuller

1895 – 1983

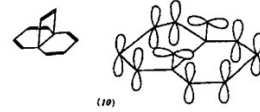


Nobelpreis für Chemie (1996): Robert F. Curl Jr., Harold W. Kroto, Richard E. Smalley

Buckminsterfulleren: Theorie



Eiji Osawa, 1994 (photograph by I. Hargittai).



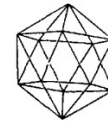
偶数系のピシコπ電子化合物は barrelene のほかには知られていないが、(4.2.2) propella-2,4,7,9,11-pentane (11)¹⁰⁾ が非常に密接な関連をもつことは構造式から明らかである。(10)においてはトリシクロ系骨格によって分子の inflexibility がピシコ系に比べてさらに増しているため図に示したようなπ電子の環なりがさらに大きいと考えられるが、これらもやはり熱力学的安定化は特別に起こっていないようである¹⁰⁾。



(10)のピニローグ(11)¹⁰⁾はまだ合成されていない。

2-3 corannulene

多数のベンゼン環の融合した型のいわゆる“融合多環式芳香族炭化水素”は典型的な平面分子である。これらの代表的なベンゼノイド芳香族が球状分子の型をとったなら超芳香族性を示さないだろうか？ たとえばサッカーボールの表面に描かれている幾何模様を思い浮かべてみよう。それは正多面体として cube のつぎに小さな正二十面体 (icosahedron) (12) の頂点を全部切り落として正五角形を出したもので、truncated icosahedron とでも称されるべき美しい多面体である(13)。四ではわかりにくいところもあるが、もし手もとにサッカーボールがあれば手にとりてながめていただくとはっきりするが、五角形(黒く塗ってある)の面には規則正しく六角形がうずまっている。一見これらの成分多角形はたいして曲がっていてもいいし、各辺はすべて同じ長さにすることができる。もしこれらの頂点を全部切



(12)

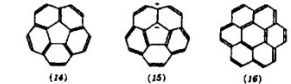


(13)

π 結合エネルギー ¹⁰⁾	
平面 corannulene	28,924
非平面 corannulene	26,306
a) $h_{\pi} = -1.7315 \text{ eV}$	

で置き換えることができれば球面状共役が実現できないだろうか？

実はこのサッカーボールの表面積の最小反復単位を切り出した形の炭化水素が合成された¹¹⁾。それが corannulene (14)である。この分子はいろいろな点で非常に興味深い。まず(15)のような dipolar 構造の共役融合体である可能性がある。というのは(15)においては同



辺が 14π 系の閉状共役。中央部が 6π 系の環状共役を形づくり、いずれも $4n+2$ 則を満たしているので強い芳香族性の発現が期待される。つきに corone (16) (平面分子)と比べてみると明らかのように(15)においてはベンゼン環が一つ足りない。したがって中央の5員環部に非常に近いはずがかり。その結果として分子が平面性を失っている可能性がある。そのアニオンラジカルの ESR スペクトルには11本の等間隔線が現れ、10個の等価なプロトンの存在することが確かめられている¹²⁾。したがってアニオンラジカル(そしてたぶん中性分子も)において非平面構造をとっているとすると、それは平面型における5回対称軸をそのまま保持した bowl 型¹³⁾あるいは basket 型¹⁴⁾とでも称すべき深い朝顔型洗面器のような形であろう。分子模型を組んでみると明らかに非平面型となり、底の5角形面とその周囲に突き出ている5本の結合とのなす角度は 38.75° にも達する。もしこのような非平面構造をとっているとすると、一体このような分子で共役安定化が可能であろうか？ この問いは(13)のような閉共役分子の存在の可否をめぐっているという意味で非常に興味深い。

この問いに答えることは実ははなはだむずかしい。たとえ水素化(まだ測定されたという報告はない)が出てもそのうちひずみによる寄与を差し引かねばならないが、その評価は一般に困難である¹⁵⁾。非経験的 MO 計算を行なうにしても分子構造パラメーターの実測値が不可欠

Buckminsterfulleren: Theorie



Elena G. Gal'pern in 1988 (courtesy of Elena Gal'pern) and Ivan V. Stankevich in 1990 (courtesy of Ivan Stankevich).

D. A. Bochvar, E. G. Gal'pern, "On hypothetical systems: carbododecahedron, s-icosahedron, and carbo-s-icosahedron", Dokl. Acad. Nauk SSSR, 1973, 209:3, 610–612

Buckminsterfulleren: GED

Kenneth Wayne Hedberg

1920 - 2019



Bond Lengths in Free Molecules of Buckminsterfullerene, C₆₀, from Gas-Phase Electron Diffraction

KENNETH HEDBERG,* LISE HEDBERG, DONALD S. BETHUNE, C. A. BROWN, H. C. DORN, ROBERT D. JOHNSON, M. DE VRIES

Electron diffraction patterns of the fullerene C₆₀ in the gaseous state have been obtained by volatilizing it from a newly designed oven-nozzle at 730°C. The many peaks of the experimental radial distribution curve calculated from the scattered intensity are completely consistent with icosahedral symmetry for the free molecule. On the basis of this symmetry assumption, least-squares refinement of a model incorporating all possible interatomic distances led to the values $r_g(\text{C}_1\text{-C}_2) = 1.458(6)$ angstroms (Å) for the thermal average bond length within the five-member ring (that is, for the bond fusing five- and six-member rings) and $r_g(\text{C}_1\text{-C}_6) = 1.401(10)$ Å for that connecting five-member rings (the bond fusing six-member rings). The weighted average of the two bond lengths and the difference between them are the values 1.439(2) Å and 0.057(6) Å, respectively. The diameter of the icosahedral sphere is 7.113(10) Å. The uncertainties in parentheses are estimated 2σ values.

RESEARCH ON THE PROPERTIES OF the molecule "buckminsterfullerene," C₆₀, has been increasing rapidly. Among the many results now available, however, there is little information about the lengths of the bonds. To date the most accurate values appear to be those from nuclear magnet-

ic resonance (NMR) work (1) (1.45 ± 0.015 Å for the bonds within the five-member ring and 1.40 ± 0.015 Å for the bonds connecting five-member rings). There are also measurements from neutron diffraction [1.44 Å (2) and 1.42 Å (3) for the weighted average distance]. All of these measurements were done on ma-

terial in condensed phases. There are also results from semiempirical and ab initio quantum mechanical calculations; the most recent of these includes the effect of electron correlation at the MP2 level and predicts the bond lengths at the 1.445 Å and 1.405 Å (4). We carried out the electron-diffraction study described here for two reasons. First, it seemed quite likely the results for the bond lengths would be more precise than any presently available, and second, these results for the gas-phase molecule would be free from the effects of intermolecular interaction that could conceivably play a role in condensed phase measurements.

Our sample of C₆₀ was produced at IBM with an arc fullerene generator (5, 6) and removed from the soot utilizing toluene in a Soxhlet extractor. The extract was purified by liquid chromatography (basic alumina) with a gradient elution system of hexane and chlorinated solvents, and characterized by NMR (7, 8) and mass spectroscopy; separation has also been obtained using a 95/5 hexane/toluene system (9).

The electron diffraction work was done at Oregon State University. In a usual type of diffraction experiment, a well-collimated,

high-energy electron beam passes through the center of an evacuated chamber and intersects a jet of gas emitted from a nozzle positioned with its tip about 1 mm from the beam and connected to a sample container outside the chamber. Because of the low volatility of C₆₀, conveyance of the vapor from outside the apparatus was unsuitable. We used instead an electrically heated nozzle-oven, fitted with a needle valve, located inside the diffraction chamber close to the electron beam. Since the temperature at which sufficient vapor pressure would be obtained for the experiment was unknown, tests for scattering were necessary. The oven was first held for about 2 hours at 200°C (a temperature known to be insufficient to volatilize the sample) with the valve open to remove any solvent remaining from the extraction process. The valve was then closed and the sample gradually heated. During the heating the valve was opened at suitable intervals to check for possible scattering that would be evident on a fluorescent screen appropriately positioned for that purpose. At about 300°C substantial scattering was seen, but it disappeared after a short interval. It is not known whether the scattering was from firmly adsorbed solvent that was not removed at 200°C, or whether it was from C₆₀. If the latter, its disappearance could be accounted for by a reduction of surface area (and consequently a much reduced rate of evaporation) caused by formation of larger crystallites (10). At about 700°C sufficient sample was being evaporated to give excellent diffraction patterns with 4- to 6-min exposures (11). Diffraction patterns were recorded at nozzle-to-plate distances of 700 and 300 mm to obtain lower- and higher-angle scattering. About 300 mg of sample was required for the production of two plates at the longer and three at the shorter camera distance.

Reduction of the data and their treatment by our usual procedures (12) led to the experimental intensity curves of Fig. 1 and the corresponding radial distribution curve of Fig. 2. If the structure has icosahedral symmetry, the geometry of the molecule is defined by only two parameters, which for convenience we chose as the radius vector from the center of the icosahedral sphere to the center of the five-member ring and the radius of the circle comprising the five-member rings. The 1770 distances between

Fig. 1. Intensity curves for C₆₀. The experimental intensity, $I_s(s)$, from each plate, amplified by a factor of 10, is shown superimposed on the background. The molecular structure-sensitive part of the experimental intensity to be compared with the theoretical curve is given by $I_{\text{net}}(s) = I_s(s)/I_0(s) - \text{background}$ [12]. The theoretical curve corresponds to the model of Table 1. The differences are experimental minus theoretical. The ordinate is intensity on an arbitrary scale, the abscissa is defined by $s = 4\pi\lambda^{-1}\sin(\theta/2)$, where θ is the scattering angle.

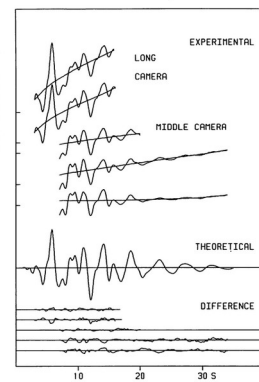


Fig. 2. Radial distribution of distance in C₆₀. The experimental curve was calculated from a composite of the experimental intensity curves shown in Fig. 1, multiplied by $\exp(-0.0020s^2)$ to minimize series termination errors. The vertical bars indicate the distances given in Table 1; their lengths are proportional to the weights of the terms. The difference curve is experimental minus theoretical (not shown).

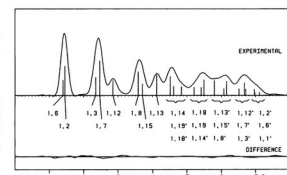


Table 1. Interatomic distances and root-mean-square amplitudes of vibration in C₆₀. The symbol r_g denotes the thermal average distance, r_s the distance consistent with the scattering equations, and l the root-mean-square amplitude of vibration. Quantities in parentheses are estimated 2σ uncertainties; those for r_g are estimated to be the same as for r_s . Amplitudes in curly brackets were refined as a group. The term numbering corresponds to that in Fig. 3.

Term	$r_s(\text{Å})$	$r_g(\text{Å})$	$l(\text{Å})$	Term	$r_s(\text{Å})$	$r_g(\text{Å})$	$l(\text{Å})$
R^*	3.332 ₂ (4 ₈)			r_{51}^\dagger	1.237 ₉ (5 ₃)		
$\langle r_{\text{bond}} \rangle^\ddagger$	1.436 (2)	1.439		$\Delta r_{\text{bond}}^\S$	0.057 (6)	0.057	
1-6	1.398 (10)	1.401	0.062 (8)	1-19	5.408 (10)	5.411	0.136 (34)
1-2	1.455 (6)	1.458	0.065 (5)	1-14'	5.491 (8)	5.494	0.133 (23)
1-3	2.355 (10)	2.357	0.080 (10)	1-13'	5.795 (8)	5.798	0.129 (18)
1-7	2.471 (5)	2.474	0.083 (7)	1-15'	6.072 (8)	6.075	0.136 (13)
1-12	2.853 (6)	2.857	0.097 (9)	1-8'	6.143 (8)	6.146	0.136 (13)
1-8	3.581 (5)	3.584	0.100 (7)	1-12'	6.513 (9)	6.516	0.144 (18)
1-15	3.699 (6)	3.702	0.099 (12)	1-7'	6.667 (9)	6.670	0.144 (18)
1-13	4.120 (6)	4.123	0.109 (8)	1-3'	6.709 (10)	6.712	0.144 (18)
1-14	4.517 (7)	4.520	0.115 (10)	1-2'	6.960 (10)	6.963	0.145 (18)
1-19'	4.617 (9)	4.619	0.106 (23)	1-6'	6.972 (10)	6.975	0.145 (18)
1-18'	4.841 (8)	4.844	0.117 (26)	1-1'	7.110 (10)	7.113	0.145 (18)
1-18	5.208 (9)	5.212	0.145 (40)				

*Structure-defining parameter: distance from center of the icosahedral sphere to center of five-member ring. †Structure-defining parameter: radius of circle comprising the five-member rings. ‡Weighted average of bond lengths. §Bond length difference.

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