Universität Bielefeld

Core Facility
GED @ Bi
Gas-Electron-Diffraction & Small Molecule Structures Centre

Mitzel Group
inorganic & structural chemistry

“Semi-experimental” structures demystified

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Universität Bielefeld

GED: Refinement of Structure

$$I_{tot} = I_{mol} + I_{at} + I_{bgl}$$

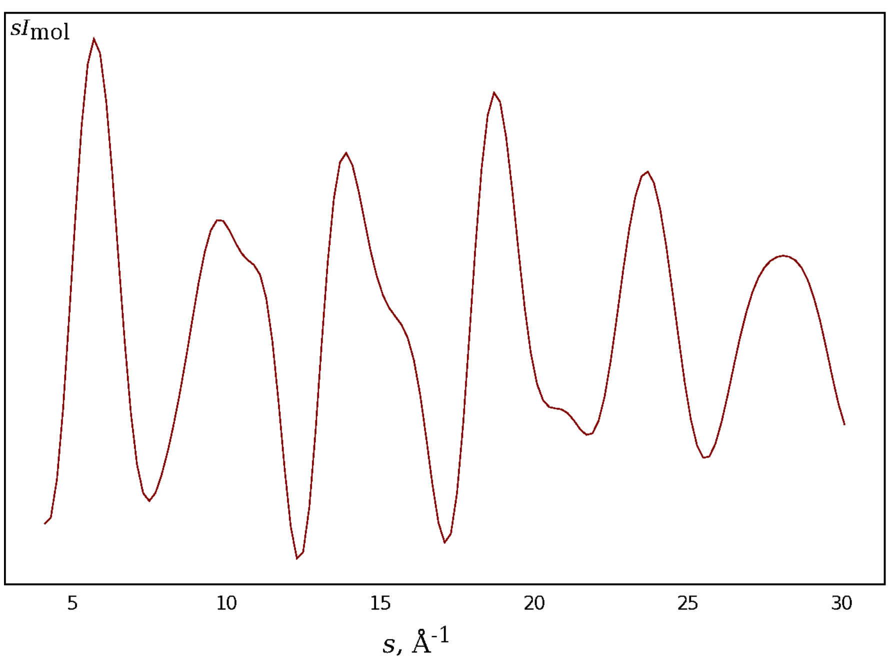
$$sM(s) = \frac{sI_{mol}}{I_{at}} = \sum_{i>j}^{N} g_{i,j} e^{-\frac{(sl_{i,j})^2}{2}} \frac{\sin(sr_{i,j} - a_{i,j} s^3)}{r_{i,j}}$$

$$s = \frac{4\pi}{\lambda} \sin\left(\frac{\theta}{2}\right)$$

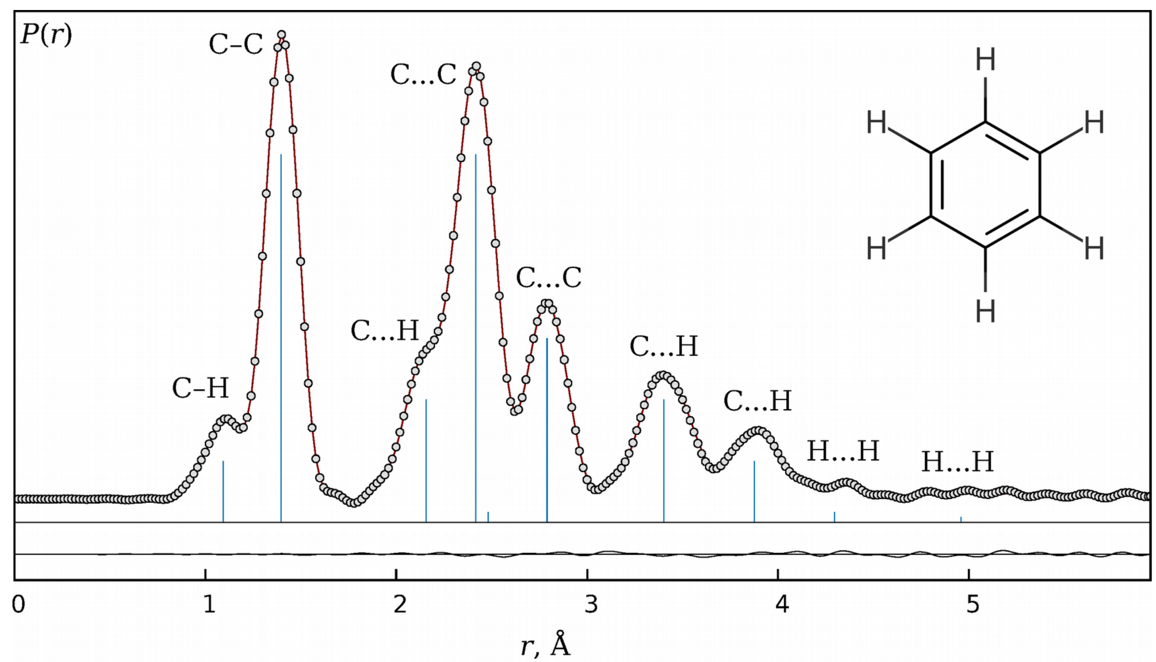
θ – scattering angle,
λ – electron wavelength,
g – scattering factors,
r – interatomic distances,
l – amplitudes,
a – asymmetry constants.

Inverse problem:

$$Q = \sum_{i}^{N} [sM(s|r,l,a)^{\exp} - sM(s)^{model}]^2 \rightarrow min$$



RDF



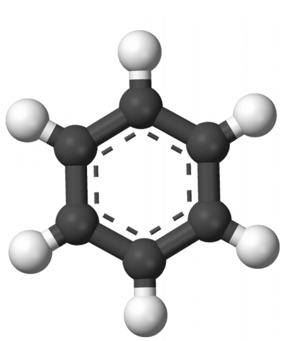
Semi-experimental structure

In most cases refined structures are in fact semi-experimental because of using supplementary theoretical data:

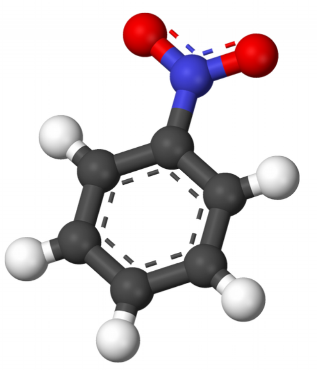
- Corrections to geometrically consistent structure (r_{h0}, r_{h1}, r_e).
- Assumed vibrational amplitudes and/or their differences.
- Assumed geometrical parameters and/or their differences.

and/or

- Regularization parameters.



vs.



How much experimental?

To which extent

is refined structure experimental

if we use supplementary theoretical data?

Lev V. Vilkov (Moscow SU)

Regularization

Tikhonov's regularization in GED: Bartel's “predicate observations”, SARACEN

Regularization of internal coordinates:

$$Q = \sum [sM(s)^{\exp} - sM(s)^{mod}]^2 + \alpha \sum_i w_i (p_i^0 - p_i^{mod})^2 \rightarrow min$$

$\alpha = 0 \longrightarrow$ Fully experimental structure (100 % experimental info. in refined prms.)

$\alpha = \infty \longrightarrow$ Fully theoretical structure (0 % exp. info. in refined prms.)

$\alpha = (0, \infty) \longrightarrow$ Semi-experimental structure (**???** %). Used in practice!

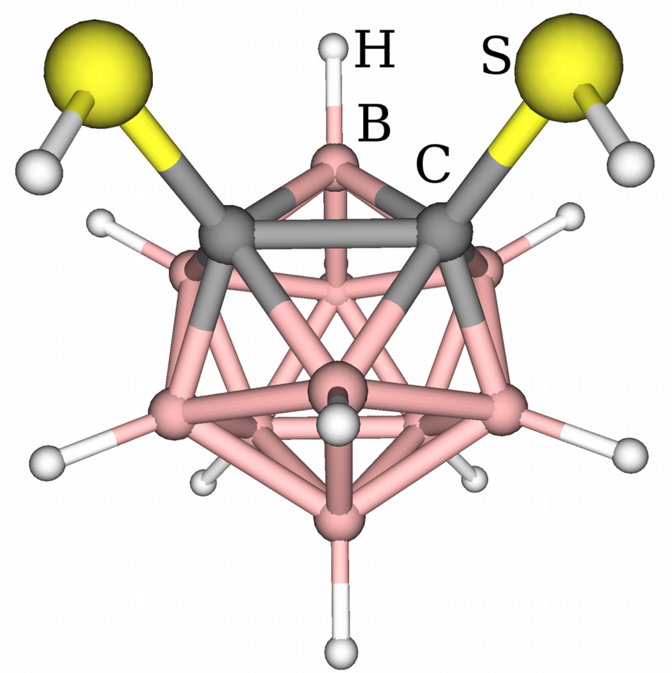
L. S. Bartell, D. J. Romenesko, T. C. Wong, in *Molecular Structure by Diffraction Methods,* The Chemical Society, London, 1975, Vol. 3, pp 72 – 79.
A. J. Blake, P. T. Brain, H. McNab, J. Miller, C. A. Morrison, S. Parsons, D. W. H. Rankin, H. E. Robertson, B. A. Smart, *J. Phys. Chem.*, 1996, 100, 12280.
A. N. Tikhonov, V. Y. Arsenin, *Solutions of Ill-posed Problems,* Washington, DC: V. H. Winston & Sons, 1977.

Example 1: *closo*-1,2-$(SH)_2$-1,2-$C_2B_{10}H_{10}$

$$Q=\sum\left[sM(s)^{\exp}-sM(s)^{mod}\right]^2+\alpha\sum_i w_i\left(x_i^0-x_i^{mod}\right)^2\rightarrow min$$

R_f = 4.3 %

α = 5.0



	MP2/cc-pVTZ	GED	
	r_e	r_e	r_g
*r*C–B	1.704	1.702(4)	1.722(4)
*r*C–C	1.756	1.755(7)	1.765(7)
*r*B–B	1.782	1.777(5)	1.793(5)
*r*C–S	1.769	1.755(4)	1.770(4)
∠B–C–B	63.4	63.3(2)	
∠B–B–B	60.0	60.0(2)	
∠S–C–C	118.0	118.0(1)	

(Semi?-) Experimental Structure?

T. Baše, P. D. Lane, Yu. V. Vishnevskiy, D. Tikhonov, C. G. Reuter, N. W. Mitzel, D. A. Wann, D. Hnyk, *Inorg. Chem.*, in preparation.

W2 Scheme

$$Q = \underbrace{\sum \left[sM(s)^{\exp} - sM(s)^{mod} \right]^2}_{Q_{GED}} + \underbrace{\alpha \sum w \left(p^0 - p^{mod} \right)^2}_{Q_{REG}} \rightarrow min$$

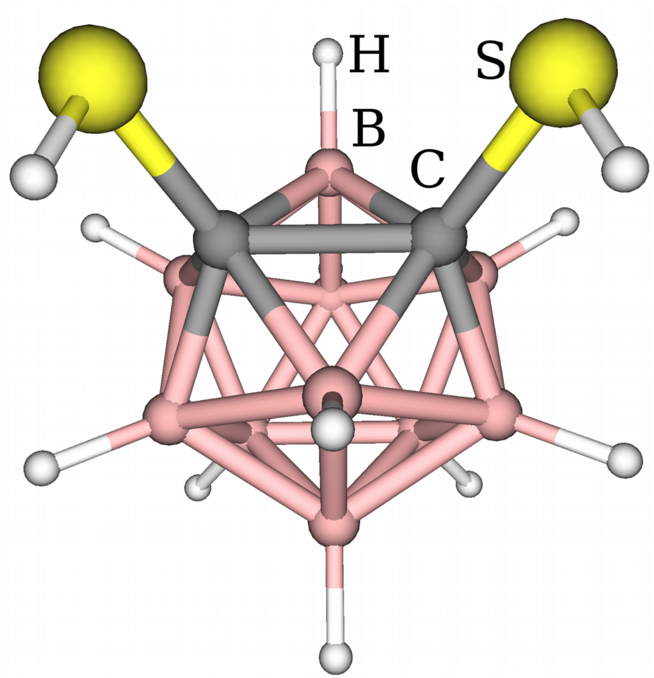
First empirical idea: use second derivatives

$$\frac{\partial^2 Q_{GED}}{\partial p^2} \qquad \frac{\partial^2 Q_{REG}}{\partial p^2}$$

$$W_{GED} = \frac{\dfrac{\partial^2 Q_{GED}}{\partial p^2}}{\dfrac{\partial^2 Q_{GED}}{\partial p^2} + \dfrac{\partial^2 Q_{REG}}{\partial p^2}}$$

D. S. Tikhonov, Yu. V. Vishnevskiy, A. N. Rykov, O. E. Grikina, L. S. Khaikin, *J. Mol. Struct.*,2017, 1132, 20–27.

closo-1,2-$(SH)_2$-1,2-$C_2B_{10}H_{10}$



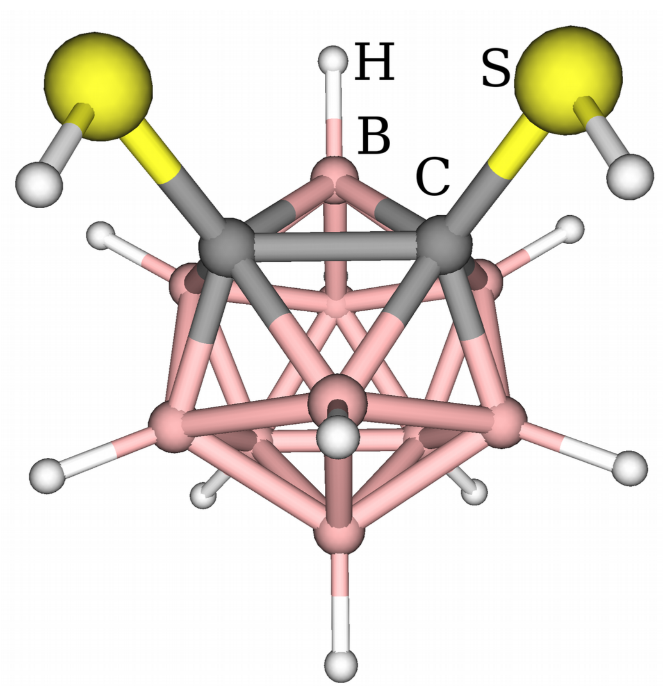
	MP2/cc-pVTZ	GED	
	r_e	r_e	w_{GED}
*r*B–H	1.181	1.186(5)	**0.001**
*r*S–H	1.339	1.341(5)	**0.007**
*r*C–B	1.704	1.702(4)	**0.168**
*r*C–C	1.756	1.755(7)	**0.079**
*r*B–B	1.782	1.777(5)	**0.176**
*r*C–S	1.769	1.755(4)	**0.357**
∠C–B–C	61.5	61.6(2)	?
∠C–B–B	58.3	58.4(2)	?
∠B–C–B	63.4	63.3(2)	?
∠B–B–B	60.0	60.0(2)	?
∠S–C–C	118.0	118.0(1)	?
∠C–B–H	116.7	116.7(3)	?
|∠CCSH(syn)|	95.2	95.2(2)	?

Angles: coincidence?

closo-1,2-$(SH)_2$-1,2-$C_2B_{10}H_{10}$

$$Q=\sum \left[sM(s)^{\exp} - sM(s)^{mod} \right]^2 + \alpha \sum_i w_i \left(x_i^0 - x_i^{mod} \right)^2 \rightarrow min$$

Uniform regularization: $w_1 = w_2 = w_3 = \ldots = 1$.



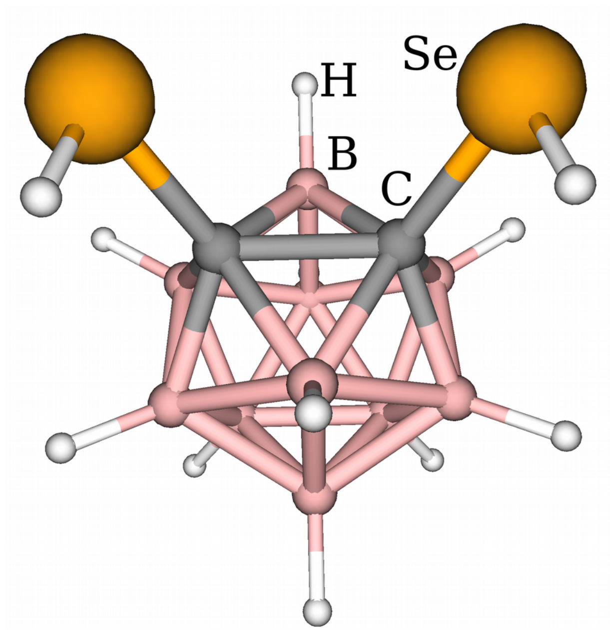
	MP2/cc-pVTZ	GED	
	r_e	r_e	w_{GED}
∠C–B–C	61.5	61.6(2)	**0.051**
∠C–B–B	58.3	58.4(2)	**0.055**
∠B–C–B	63.4	63.3(2)	**0.053**
∠B–B–B	60.0	60.0(2)	**0.036**
∠S–C–C	118.0	118.0(1)	**0.128**
∠C–B–H	116.7	116.7(3)	**0.015**
|∠CCSH(syn)|	95.2	95.2(2)	**0.000_7**

Low w_{GED} for Angles!

Want more “experiment” in parameters?

No problem, decrease α, but be ready to pay for this!

$$Q=\sum\left[sM(s)^{\exp}-sM(s)^{mod}\right]^2+\alpha\sum_i w_i\left(x_i^0-x_i^{mod}\right)^2\rightarrow min$$



	MP2/ cc-pVTZ	GED			
		α = 0.7		α = 43	
	r_e	r_e	w	r_e	w
rC–C	1.731	1.750(28)	**0.933**	1.726(5)	**0.172**
rB–B	1.782	1.777(19)	**0.943**	1.775(3)	**0.236**
rC–Se	1.904	1.902(10)	**0.987**	1.904(3)	**0.521**
∠Se–C–C	119.2	119.2(4)	**0.971**	119.3(1)	**0.319**
∠Se–C–B	118.9	119.1(9)	**0.908**	118.9(2)	**0.172**
∠B–B–H	123.1	123.0(12)	**0.506**	123.1(2)	**0.016**
R_f, %	10.8	4.0		5.1	

T. Baše, P. D. Lane, Yu. V. Vishnevskiy, D. Tikhonov, C. G. Reuter, N. W. Mitzel, D. A. Wann, D. Hnyk, *Inorg. Chem.*, in preparation.

More Theory: W12 Scheme

General form of functional:

$$\Phi = \sum_i \Phi_i \rightarrow min$$

Associated distributions (Gaussian approximation):

$$p_i = \frac{1}{\sqrt{2\pi}\,\sigma_i} \exp\left(\frac{-(\xi - \mu_i)^2}{2\sigma_i^2}\right)$$

Kullback-Leibler divergence:

$$J(f_1, f_2) = \int f_1 \ln\left(\frac{f_2}{f_1}\right) dx + \int f_2 \ln\left(\frac{f_1}{f_2}\right) dx$$

Derivatives:

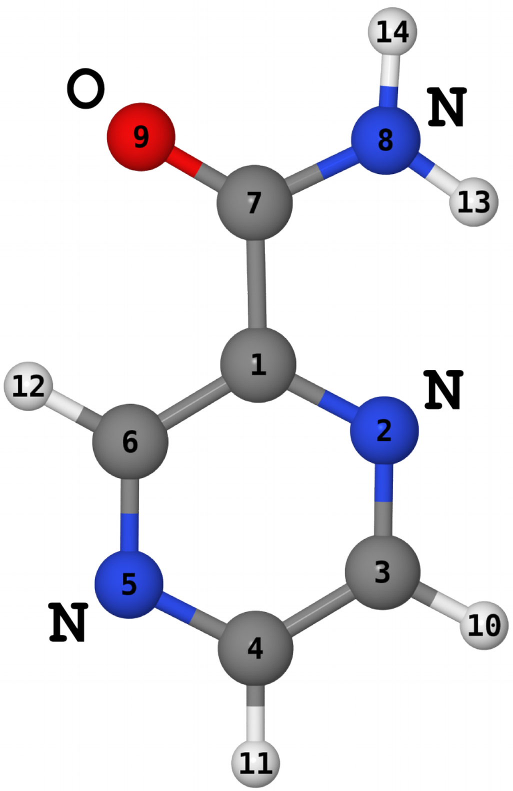
$$a_i^{(k)} = \frac{\partial^k \Phi_i}{\partial \xi^k} \qquad a^{(k)} = \sum_i a_i^{(k)}$$

$$J(p_i, p) = \frac{1}{2}\left[\left(\frac{a_i^{(1)}}{a_i^{(2)}} - \frac{a^{(1)}}{a^{(2)}}\right)^2 (a_i^{(2)} + a^{(2)}) + \frac{a^{(2)}}{a_i^{(2)}} + \frac{a_i^{(2)}}{a^{(2)}} - 2\right]$$

$$w_i = \frac{\frac{1}{J(p_i, p)}}{\sum_j \frac{1}{J(p_j, p)}} = \frac{1}{1 + J(p_i, p) \sum_{j \neq i} \frac{1}{J(p_j, p)}}$$

S. Kullback, R. A. Leibler, *Ann. Math. Stat.*, 22, 1951, 79.
D. S. Tikhonov, Yu. V. Vishnevskiy, A. N. Rykov, O. E. Grikina, L. S. Khaikin, *J. Mol. Struct.*,2017, 1132, 20–27.

W12 vs. W2: Pyrazinamide



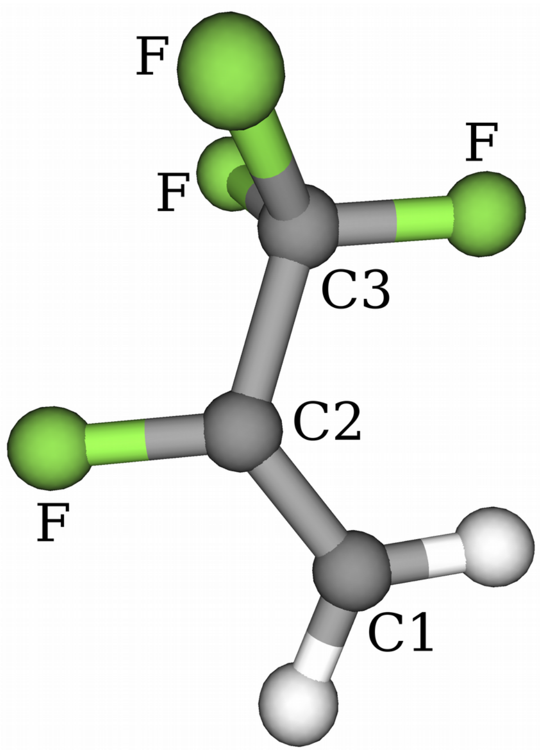
	MP2(full)/ cc-pwCVTZ	GED		
	r_e	r_e	$w12$	$w2$
rC1–N2	1.336	1.341(2)	**1.00**	**0.96**
rC1–C6	1.391	1.404(2)	**1.00**	**0.96**
rC3–H10	1.081	1.082(4)	**0.02**	**0.21**
∠N2–C3–C4	122.0	122.1(2)	**0.90**	**0.68**
∠N8–C7–O9	125.2	124.9(2)	**1.00**	**0.88**
$\angle(\text{X–C3–H10})_{av}$	119.1	119.0(3)	**0.26**	**0.39**
∠H13–N8–H14	121.8	121.8(3)	**0.00**	**0.03**

Consistent results

D. S. Tikhonov, Yu. V. Vishnevskiy, A. N. Rykov, O. E. Grikina, L. S. Khaikin, *J. Mol. Struct.*,2017, 1132, 20–27.

GED Data + Rotational Constants

$$Q = \underbrace{\sum \left[sM(s)^{exp} - sM(s)^{mod} \right]^2}_{Q_{GED}} + \underbrace{\alpha \sum w \left(B^{exp} - B^{mod} \right)^2}_{Q_{ROT}} \rightarrow min$$



Parameter	Calcd.	MW	GED	GED+MW	w_{GED}
*r*C1–C2	1.323	1.319(2)	1.324(1)	1.317(1)	**0.15**
*r*C2–C3	1.503	1.503(2)	1.494(1)	1.497(1)	**0.15**
*r*C2–F	1.335	1.333(1)	1.333(1)	1.334(1)	**0.23**
$r(\text{C3–F})_{\text{av}}$	1.333	1.333(1)	1.334(1)	1.335(1)	**0.23**
$r(\text{C1–H})_{\text{av}}$	1.078	1.070(29)	1.098(4)	1.085(3)	**0.36**
∠C1–C2–C3	125.9	126.1(1)	124.7(1)	125.8(1)	**0.22**
φC1–C2–C3–F	120.3	120.5(1)	121.5(1)	120.5(1)	**0.02**
R_f, %			4.45	4.72	

Calcd. = full-CCSD(T)/cc-pwCVTZ

GED+MW: $|B^{exp} - B^{mod}|$ were approx. 1% of *d*B.

M. D. Marshall, H. O. Leung, B. Q. Scheetz, J. E. Thaler, J. S. Muenter, *J. Mol. Spectr.*, 266, 2011, 37-42.

Thank you for your attention!