

A Theoretical Study of the Equilibrium Conformations and the Barrier to Internal Rotation in Some Fluorobiphenyls

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The equilibrium conformations and the barriers to internal rotation in a series of fluorine substituted biphenyls have been estimated by a combined study of conjugation energy and non-bonded interactions. The importance of each of these terms is discussed. The predicted equilibrium conformations are in fair agreement with available experimental information.

The equilibrium conformation and the barrier to internal rotation in biphenyl and its derivatives have been extensively studied by experimental investigations and by theoretical calculations.

Electron diffraction studies of biphenyl¹ itself and a series of its derivatives²⁻⁵ have all led to the conclusion that in the vapour phase these molecules have a non-planar equilibrium conformation. For biphenyl itself and some *meta*- and *para*-substituted derivatives the angles between the planes defined by the phenyl rings are found to be around 45°. For *ortho*-substituted derivatives the angle is found to be larger, its actual value being dependent on the nature of the substituent.⁵

The purpose of the present investigation is to study the equilibrium conformations and barriers to internal rotation of a series of *ortho*-substituted fluorobiphenyls. The computational method applied is similar to an approach used in corresponding studies previously. The gross features of the method may be characterized by a decomposition of the molecular energy into conjugation energy and non-bonded interactions. By a systematic variation of the number of substituents, and of their mutual positions, a discussion of the relative importance of these two energy terms was possible.

Of the five different molecules studied here only two have been investigated experimentally in the vapour phase, namely 2-fluorobiphenyl³ and 2,2'-difluorobiphenyl.³ The recently studied geometry of decafluorobiphenyl⁵ is considered to be an adequate model for a discussion of our predicted equilibrium conformation of 2,6,2',6'-tetrafluorobiphenyl. For the remaining molecules included in our calculations, 2,6-difluorobiphenyl and 2,6,2'-trifluorobiphenyl, no experimental gas phase data are available to the authors' knowledge.

DETERMINATION OF PARAMETERS FOR THE π -ELECTRON SYSTEM

The total energy of the molecules has been assumed to be decomposed into conjugation energy and non-bonded interactions. The conjugation energy is furthermore considered as composed of the π -electron energy and the core-energy. The first of these terms was calculated within the ZDO (zero differential overlap) approximation, using a scheme of parametrization previously introduced and discussed.⁶ A tentative set of parameter-values for F and for the C-F bond has been evaluated within the same scheme, and applied in the calculation of the π -electron energies.

In the following a brief sketch of the evaluation of the semi-empirical parameters for the F atom and for the C-F bond will be given. For details concerning the method itself and for the remaining parameters appropriate to the π -electron system, see Refs.^{6,7}

The parameters to be determined semi-empirically are:

$$\beta_{C-F} = \beta_{C-F}^{\circ} + \delta_{CF}^{\beta}(R_{CF} - R_{CF}^{\circ}) \quad (1)$$

$$\gamma_{C-F} = \gamma_{C-F}^{\circ} + \delta_{CF}^{\gamma}(R_{CF} - R_{CF}^{\circ}) \quad (2)$$

$$W_F = W_F^{\circ} + \delta_{CF}^W(R_{CF} - R_{CF}^{\circ}) \quad (3)$$

and $\Delta W_C^{\circ}(F)$ in

$$W_C = W_C^{\circ} + \sum_{\nu=1}^3 n_{\nu}[\Delta W_C^{\circ}(\gamma) + \delta_{C\nu}^W(R_{C\nu} - R_{C\nu}^{\circ})] \quad (4)$$

In (1) β_{C-F}° is the value of the core resonance integral at a chosen reference distance R_{CF}° , and δ_{CF}^{β} is a proportionality constant which is assumed to be equal to its counterpart in a carbon-carbon bond. Formula (2) presents a corresponding relation assumed for the two-electron two-center coulomb integrals appropriate to bond distances. The value of δ_{CF}^{γ} has also been assumed equal to the corresponding value for a carbon-carbon bond. The same is also the case for δ_{CF}^W in (3) and (4). In (4) n_{ν} is equal to zero if the neighbouring atom ν to C is a hydrogen atom and equal to unity otherwise. As the parameters appropriate to the C-C bonds are known from previous studies, and the actual bond distances are known or assumed, the only parameter to be determined in (4) is $\Delta W_C^{\circ}(F)$.

Thus due to the assumptions made there are altogether four parameters to be determined: β_{C-F}° , γ_{C-F}° , W_F° , and $\Delta W_C^{\circ}(F)$.

The value $R_{CF}^{\circ} = 1.340 \text{ \AA}$ has been adopted in all the expressions above.

The experimental information applied in the numerical evaluation of the semi-empirical parameters were the observed electronic transition energies and π -electron ionization potentials for fluorobenzene, 1,4-difluorobenzene, and 1,2,4-trifluorobenzene. Furthermore measured ionization potentials for vinylfluoride, 2,2-difluoroethylene, and tetrafluoroethylene were taken into consideration. At the time when this investigation was carried through, the recently published vapour spectra¹⁴ of the fluoroethylenes were not available.

The transition energies for the fluorobenzenes applied by the adjustment of the parameters were arrived at by using the published shifts⁸ of the corresponding vertical benzene transitions. For all the fluorobenzenes the data

related to the 1L_b band refer to measurements in vapour, whereas the data for the 1L_a and 1B bands in monofluorobenzene refer to solution spectra.

For the fluorobenzenes we have applied experimental ionization potentials obtained by photoelectron spectroscopy,⁹ whereas photoionization values have been used for the fluoroethylenes.¹⁰

By the adjustment of the parameters it was experienced that rather large changes in their numerical values could be permitted without changing the predicted transition energies and ionization potentials significantly. This was particularly true for the parameter γ_{C-F}° .

The final parameter set arrived at is presented in Table 1. In Table 2 is given a comparison between predicted values and the measured values used by the adjustment. It might be mentioned that an alternative set of parameters deviating rather much from the first one, as indicated by the values given in parentheses in Table 1, gave an agreement with observations which was as good as for the first one. The predicted values using this alternative set are included in parentheses in Table 2.

Table 1. Semi-empirical parameters for the C—F bond. All values in eV. For notation, see text.

$\gamma_{FF} = 22.36$	$\beta_{CF}^\circ = -1.30$	$(-1.20)^a$
$\gamma_{CF}^\circ = 6$	$W_F^\circ = -11.08$	$(-12.13)^a$
	$\Delta W_{C^\circ}(F) = -1.18$	

^a Alternative set of parameter values leading to the predicted values given in parentheses in Table 2.

Table 2. Comparison between calculated^a and experimental data applied in the evaluation of the semi-empirical parameters. All values in eV.

Molecule	(IP) _{calc.}	(IP) _{obs.}	$\Delta E_{calc.}$	$\Delta E_{obs.}$
Fluorobenzene	9.21(9.23)	9.21 ^b	4.80(4.79)	4.86 ^d
	9.23(9.24)		6.08(6.03)	6.25 ^d
			6.84(6.76)	6.97 ^d
1,4-Difluorobenzene	9.19(9.21)	9.15 ^b	4.73(4.73)	4.74 ^d
1,2,4-Trifluorobenzene	9.22(9.24)	9.30 ^b	4.68(4.68)	4.78 ^d
	9.17(9.20)			
Vinylfluoride	9.18(9.23)	10.27(10.37)		
1,1-Difluoroethylene	10.27(10.37)	10.37 ^c		
Tetrafluoroethylene	10.35(10.21)	10.30 ^c		
	10.21(10.18)	10.12 ^c		

^a Calculated values in parentheses refer to the alternative parameter set given in Table 1.

^b Ref. 9; ^c Ref. 10; ^d Ref. 8.

The reason for choosing the first set characterized by the rather low value of γ_{C-F}° , is that this value seems to fit rather well in a systematic variation of parameter values considered as functions of orbital exponents.¹¹

The uncertainty in the value of this and also of the other parameters entering the π -electron calculations should not influence the estimation of equilibrium conformations and barriers to internal rotation to any significant extent.

For the one-center two-electron integrals we have adopted values previously determined by one of us.¹² The values are 11.97 eV and 22.36 eV for C and F, respectively.

The two-electron integrals for non-nearest neighbours were estimated by the uniformly charged sphere approximation, using diameters of the spheres based on the orbital exponents of Duncanson and Coulson.¹³

Since this investigation was completed, experimental values for the vapour phase transitions in the fluoroethylenes were reported.¹⁴ Refinements of our parameters taking this additional information into account are in progress.¹⁵ Preliminary results of this refinement show that the changes in our parameters will be very small.

THE ROTATIONAL BARRIERS IN THE BIPHENYLS

The equilibrium conformations and the barriers to internal rotation in the fluorine-substituted biphenyls, shown in Fig. 1, were calculated by considering the variation of the π -electron energy, the core energy, and the non-bonded interactions as functions of the angle of rotation around the central carbon-carbon bond, $C_1-C_{1'}$.

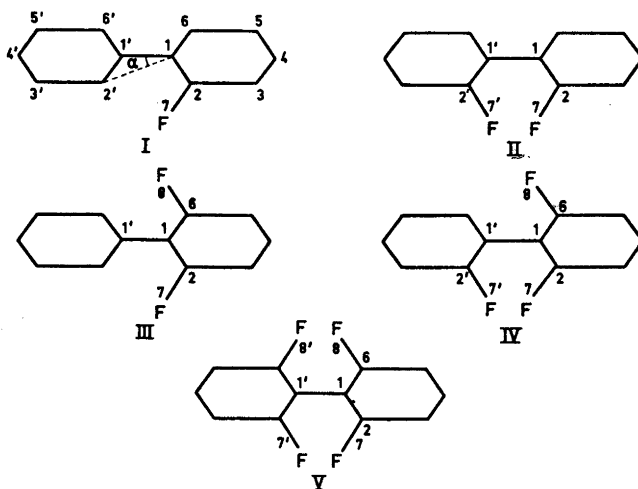


Fig. 1. Numbering of molecules and labelling of atoms. (I) 2-Fluorobiphenyl, (II) 2,2'-difluorobiphenyl, (III) 2,6-difluorobiphenyl, (IV) 2,2',6-trifluorobiphenyl, and (V) 2,2',6,6'-tetrafluorobiphenyl.

The variation of each of these energy terms will be treated separately.

During rotation all bond distances and valence angles were kept unchanged.

The chosen values of the structure parameters of this type were 1.397 Å for all C–C bonds except for C₁–C_{1'}, which was assumed to be 1.51 Å. In all the molecules the C–F bond lengths were taken to be 1.34 Å.

The values of the one-electron integrals W_μ , and of all the core-resonance integrals except $\beta_{1-1'}$, were kept constant during the rotation. The last one was varied according to the usual relation

$$\beta_{1-1'}(\phi) = \beta_{1-1'}(0) \cdot |\cos \phi| \quad (5)$$

where ϕ is the angle of rotation.

The two-electron integrals have been divided into groups according to their behaviour under rotation of the phenyl rings.

The only integrals of this kind that change during rotation are those involving one atom in each of the phenyl groups. The remaining ones have been treated by standard methods used for planar systems. Those for the bond distances were estimated according to the linear relations discussed above, and the other ones have been evaluated by means of the uniformly charged sphere approximation.

The integrals varying with the angle of rotation may be expressed in the following way:

$$\begin{aligned} (\mu\mu|\nu\nu)_\phi = & C_{xx}^{xx}(\mu_x\mu_x|\nu_x\nu_x) + C_{xx}^{zz}(\mu_x\mu_x|\nu_z\nu_z) + C_{yy}^{xx}(\mu_x\mu_x|\nu_y\nu_y) \\ & + C_{zz}^{xx}(\mu_x\mu_x|\nu_z\nu_z) + C_{xx}^{zz}(\mu_x\mu_x|\nu_x\nu_x) + C_{xy}^{xy}(\mu_x\mu_y|\nu_x\nu_y) + C_{xz}^{zz}(\mu_x\mu_z|\nu_x\nu_z) \end{aligned} \quad (6)$$

where μ and ν represent $2p$ -orbitals centered at atoms μ and ν , respectively. The mutually orthogonal x - and y -axes are vertical to the z -axes which coincide with the straight line connecting the atoms during rotation. Furthermore, the x -axes are kept orthogonal to the respective ring planes.

The coefficients are parameters determined by the molecular geometries, and they are functions of the angle ϕ . For $\phi = 0^\circ$ we have $C_{xx}^{xx} = 1$ and the remaining coefficients vanish identically.

In the cases where the distance between the atoms does not change by rotation, we obtain the simplified expression:

$$\begin{aligned} (\mu\mu|\nu\nu)_\phi = & \cos^2\phi(\mu_x\mu_x|\nu_x\nu_x) + \sin^2\phi\cos^2\alpha(\mu_x\mu_x|\nu_y\nu_y) \\ & + \sin^2\phi\sin^2\alpha(\mu_x\mu_x|\nu_z\nu_z) \end{aligned} \quad (7)$$

The angle α is defined in Fig. 1 for the case where μ is centered at C₁ and ν is centered at C_{2'}.

The integrals on the righthand side of (6) and (7) have been estimated in the following way: The theoretically calculated values of these integrals based on the orbital exponents of Duncanson and Coulson were scaled by the following relation:

$$(\mu\mu|\nu\nu)_{\text{scaled}} = (\mu\mu|\nu\nu)_{\text{th.}} \frac{(\mu_x\mu_x|\nu_x\nu_x)_{\text{ball}}}{(\mu_x\mu_x|\nu_x\nu_x)_{\text{th.}}} \quad (8)$$

where $(\mu_x\mu_x|\nu_x\nu_x)_{\text{ball}}$ is the value of the pure π -component estimated by the uniformly charged sphere approximation.

As this technique is rather laborious, we have also estimated the integrals by a modified version of the uniformly charged sphere approximation valid for non-parallel p -orbitals.¹⁶

Table 3. Comparison between values of two-electron integrals obtained by the two different methods discussed in the text. All values in a.u.

Integral	Method	Angle of rotation				
		0°	30°	60°	90°	120°
(77 2'2')	eqn.(8)	0.1992	0.1928	0.1727	0.1509	0.1349
	Ref. 16	0.1992	0.1926	0.1743	0.1526	0.1357
(77 1'1')	eqn. (8)	0.1795	0.1814	0.1853	0.1873	
	Ref. 16	0.1795	0.1822	0.1880	0.1912	

To obtain a test of the consistency of these two methods, we have calculated the integrals (77|2'2') and (77|1'1') by both methods at different angles. The results, which are presented in Table 3, show that there is a good agreement between values obtained by these two different approaches. The accordance will be even better for cases where the internuclear distance is larger. Accordingly we have adopted the modified uniformly charged sphere approximation for the calculation of the two-electron two-center integrals over non-neighbouring atoms.

The integral $(11|1'1')_{\phi}$ has been treated in a special way. By decomposing in the same manner as described above, we obtain

$$(11|1'1')_{\phi} = \cos^2\phi(1_x1_x|1_x'1_x') + \sin^2\phi(1_x1_x|1_y'1_y') \quad (9)$$

For Slater-type orbitals the following relation is valid

$$(1_x1_x|1_y'1_y') = (1_x1_x|1_x'1_x') - 2(1_x1_y|1_x'1_y') \quad (10)$$

The component $(1_x1_x|1_x'1_x')$ has been estimated by the linear formula assumed for nearest neighbours. For the integral $(1_x1_y|1_x'1_y')$, which is very small at the actual distance, we have adopted a theoretical value based on the orbital exponents referred to above.

In 2,2'-difluorobiphenyl the distance between the fluorine atoms is only 1.57 Å in the planar *cis*-form of the molecule. By rotation to $\phi = 30^\circ$ this distance is increased to 1.99 Å. For both these distances the uniformly charged sphere approximation is considered to be inadequate. However, we have estimated the coulomb integral between the fluorine atoms by this approximation to be 0.3150 a.u. in the planar molecule, and we have also carried through calculations by assuming the significantly lower value of 0.2500 a.u. The sums of π -electron energy and core energy calculated by these two different methods differ by 0.05 kcal/mole. The same difference was obtained for $\phi = 30^\circ$. Thus for our purposes the uniformly charged sphere approximation seems to be an

adequate procedure for evaluating this integral. Accordingly this method has been applied in this case and also for the other ones where this type of integral occurs.

The most realistic way of accounting for the repulsion between the positively charged core atoms is to represent it by the sum of the two-electron two-center integrals. By this method inaccuracies in the values of the two-electron integrals will not influence the predicted value of the total electronic energy to any significant extent. See the discussion in the preceding paragraph.

Several potential functions for the calculation of van der Waals interactions between non-bonded atoms have been suggested in the literature. We have here applied the well-known formula due to Hill.¹⁷

$$E_{\text{nb}} = \sum_{k < l} \{ 8.28 \times 10^5 \times \varepsilon_{kl} \exp[-r_{kl}/0.0736(R_k + R_l)] - 2.25 \varepsilon_{kl} [(R_k + R_l)/r_{kl}]^6 \} \quad (11)$$

where R_k and R_l are the van der Waals radii for atoms k and l respectively, and where ε_{kl} is a parameter specific to each atom pair. The numerical values of these parameters and of the appropriate van der Waals radii were taken from a compilation by Eliel *et al.*¹⁸

RESULTS AND DISCUSSION

The total π -electron energies are given by

$$E_{\pi} = \sum_i [\varepsilon_i + \langle \psi_i | H^{\text{core}} | \psi_i \rangle] \quad (12)$$

where ε_i are the eigenvalues of the self-consistent Fock operator, and where $\langle \psi_i | H^{\text{core}} | \psi_i \rangle$ are matrix elements in the molecular orbital representation.

The energy that is of importance in the present discussion is the sum of E_{π} and the core-repulsion energy which is approximated by the two-electron integrals:

$$E = E_{\pi} + E^{\text{core}} = E_{\pi} + \sum_{i > j} \gamma_{ij} \quad (13)$$

As both E_{π} and E^{core} vary by changing conformations of the molecules, E given by (13) will be a function $E(\phi)$ of the angle of rotation around the bond $C_1 - C_1'$.

The conjugation energy is obtained from the relation:

$$E_{\text{conj.}}(\phi) = E(\phi) - E(90^\circ) \quad (14)$$

For all molecules except 2,2'-difluorobiphenyl, the function $E(\phi)$ is symmetric around $\phi = 90^\circ$. Values of $E_{\text{conj.}}(\phi)$ are given in Table 4 for steps of 30° in the angle ϕ .

The variation in the van der Waals interactions for the same rotational steps are also included, as well as the variation in the total energies $E_t(\phi)$.

From the data given in the table we can extract the following results:

Molecule (I) has an energy minimum at around 30° rotation from the planar form. This angle is somewhat smaller than the one measured,³ namely $49 \pm 5^\circ$. Our value is even lower than the one observed in gaseous biphenyl

Table 4. Conjugation energy, variation in non-bonded interactions and in total energy. Energy values in kcal/mole.

Molecule	Type of energy	$\phi=0^\circ$ (cise)	$\phi=30^\circ$	$\phi=60^\circ$	$\phi=90^\circ$	$\phi=120^\circ$	$\phi=150^\circ$	$\phi=180^\circ$
2-Fluorobiphenyl (I)	$E_{\text{conj}}(\phi)$ from (14)	-12.3	-9.1	-3.1	0			
	$E_{\text{nb}}(90^\circ) - E_{\text{nb}}(\phi)$	+ 6.6	+1.1	0.0	0			
	$E_t(90^\circ) - E_t(\phi)$	- 5.7	- 8.0	- 3.0	0			
2,6-Difluorobiphenyl (III)	$E_{\text{conj}}(\phi)$ from (14)	-12.3	-9.2	-3.1	0			
	$E_{\text{nb}}(90^\circ) - E_{\text{nb}}(\phi)$	+10.9	+1.6	0.0	0			
	$E_t(90^\circ) - E_t(\phi)$	- 1.4	- 7.6	- 3.1	0			
2,6,2'-Trifluorobiphenyl (IV)	$E_{\text{conj}}(\phi)$ from (14)	-12.0	-9.1	-3.0	0			
	$E_{\text{nb}}(90^\circ) - E_{\text{nb}}(\phi)$	+34.3	+4.0	-0.1	0			
	$E_t(90^\circ) - E_t(\phi)$	+22.3	-5.1	-3.1	0			
2,6,2',6'-Tetrafluorobi- phenyl (V)	$E_{\text{conj}}(\phi)$ from (14)	-12.0	-9.0	-3.1	0			
	$E_{\text{nb}}(90^\circ) - E_{\text{nb}}(\phi)$	+57.7	+6.3	-0.1	0			
	$E_t(90^\circ) - E_t(\phi)$	+45.7	-2.7	-3.2	0			
2,2'-Difluorobiphenyl (II)	$E_{\text{conj}}(\phi)$ from (14)	-12.2	-9.2	-3.0	0	-3.1	-9.1	-12.3
	$E_{\text{nb}}(90^\circ) - E_{\text{nb}}(\phi)$	+30.1	+3.5	0.0	0	+0.1	+1.7	+11.0
	$E_t(90^\circ) - E_t(\phi)$	+17.9	-5.7	-3.0	0	-3.0	-7.4	- 1.3

itself.¹ On the other hand we find a definite minimum in the total energy for a non-planar conformation of the molecule.

The conformation of biphenyl itself has been studied previously by the same approach.¹⁹ The results obtained differ somewhat from ours. First of all the predicted equilibrium angle for biphenyl was in good agreement with the observed one. A comparison between the calculated values for conjugation energy and non-bonded interactions shows that the conjugation energy in our case is found to be -12.3 kcal/mol whereas the corresponding value for biphenyl is -6.2 kcal/mol. For the non-bonded interactions the differences between $\phi = 90^\circ$ and $\phi = 0^\circ$ are -6.6 kcal/mol and -4.8 kcal/mol for the two molecules, respectively. The much larger conjugation energy predicted for the fluoro-derivative tends to favour the planar form, and explains our low value for the optimal angle of twist. An alternative potential for the H-H interactions in the case of biphenyl changed this contribution to -9.9 kcal/mol.¹⁹

Thus we may conclude that the prediction of a rotation angle on the lower side of the observed one mainly is due to a rather large calculated conjugation energy in the system.

The predicted value of the barrier to internal rotation in this molecule is around 8 kcal/mol. The height of this barrier is almost exclusively determined by the conjugation energy. The corresponding value in biphenyl itself is predicted to be around 3 kcal/mol.¹⁹

For molecule (III) we find a minimum in the total energy for an angle which is somewhat larger than in molecule (I). This is to be expected due to the presence of two fluorine atoms in *ortho* position to the bridge bond. The potential minimum in this case is found in the region $30^\circ - 35^\circ$, and the magnitude of the barrier is estimated to be around 8 kcal/mol. The contribution to this barrier from non-bonded interactions is found to be roughly the same as in the previous case.

In molecule (IV) the situation is somewhat different. The conjugation energy is roughly the same as in the previous cases, whereas the non-bonded interactions play a more important part, and contribute significantly to the barrier which is about 27 kcal/mol. The energy maximum in this case is for the planar form. Due to the behaviour of the non-bonded potential function, the minimum for the total energy is rather shallow, and extends from around 30° to about 45° .

The last molecule having a symmetry around $\phi = 90^\circ$ is (V). Also here the conjugation energy is the same as in the previous cases, but the non-bonded interaction energy has a variation yielding a total energy curve that shows an extremely slow variation in the region $\phi = 30^\circ$ to $\phi = 60^\circ$. The minimum is located at around 60° , and the barrier to internal rotation is estimated to be about 49 kcal/mol. To the authors' knowledge there is no experimental determination of the vapour phase structure of this molecule available. However, a very recent electron diffraction study of the molecular structure of decafluorobiphenyl has been carried through yielding an equilibrium angle of around 70° .⁵ In the same study the energy difference between the conformers defined by $\phi = 90^\circ$ and $\phi = 70^\circ$ was estimated to be $0.4 - 2.0$ kcal/mol. The corresponding difference predicted here is around 3 kcal/mol.

The only molecule in this series which has to be investigated in the ϕ -range 0° to 180° due to lack of symmetry is (II). For this molecule we find two energy minima, one at around 45° from the planar *cis*-form, and another at about 150° . These two minima show practically the same energy, the difference being around 1.5 kcal/mol. The energy difference between these conformers and the one corresponding to $\phi = 90^\circ$ is found to be around 8 kcal/mol. The planar form has an estimated energy which is about 25 kcal/mol above the deepest minimum. This is about half of the value predicted for molecule (V).

An electron diffraction investigation gives as a result that this molecule has a non-planar *cis*-conformation where the angle of rotation is around 60° .³ However, a reinspection of the experimental radial distribution function shows that there might be a mixture of molecules having *cis*- and *trans*-conformations with the equilibrium towards the *cis*-conformer.⁵ A reinvestigation of the molecule by electron diffraction is in progress.²⁰

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