Localization of Two Phylloquinones, QK and QK', in an Improved Electron Density Map of Photosystem I at 4-Å Resolution*

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An improved electron density map of photosystem I from Synechococcus elongatus calculated at 4-Å resolution for the first time reveals a second phylloquinone molecule and thereby completes the set of cofactors constituting the electron transfer system of this iron-sulfur type photosynthetic reaction center: six chlorophyll a, two phylloquinones, and three Fe₄S₄ clusters. The location of the newly identified phylloquinone pair, the individual plane orientations of these molecules, and the resulting distances to other cofactors of the electron transfer system are discussed and compared with those determined by magnetic resonance techniques.

The electron transfer processes of oxygenic photosynthesis, as observed in cyanobacteria, eukaryotic algae, and higher plants, involve two distinct types of photosynthetic reaction centers located in the thylakoid membrane. Photosystem II catalyzes the light-driven luminal oxidation of water and the reduction of plastoquinone near the stromal side of the photosynthetic membrane. Photosystem I (PSI)* luminally oxidizes the soluble electron donor plastocyanin (alternatively cytochrome b₅₆₅) and stromally reduces the extrinsic electron acceptor ferredoxin or flavodoxin. The reduced ferredoxin induces the reduction of NADP⁺, a reaction catalyzed by ferredoxin:NADP⁺ reductase. Photosystem I receives electrons from photosystem II via an intermediate plastoquinone pool, the cytochrome b₅₆₅ complex, and water soluble electron carriers. The difference in proton concentration across the thylakoid membrane, which results from the proton pumping of the plastoquinone pool and the cytochrome b₅₆₅ complex, the stromal consumption of protons by NADP⁺ reduction, and the luminal release of protons following water oxidation, is used by the ATP-synthase for phosphorylation of ADP to ATP (1, 2).

Cyanobacterial PSI consists of 11 subunits referred to as PsAA to PsAF and PsAI to PsAM. An x-ray structural model of a cyanobacterial PSI complex from the thermophile Synechococcus elongatus has been postulated on the basis of an electron density map calculated at 4-Å resolution (3, 4). Despite the comparatively low resolution, it was possible to suggest an assignment of 43 α-helices to the individual subunits of PSI by correlating the information provided by the electron density map with available biochemical and biophysical data. Furthermore, the electron density map allowed the positioning of 89 Chl a molecules, constituents of both the core antenna system and electron transfer system, one phylloquinone, and three iron-sulfur clusters to be modeled.

The electron transfer reactions of PSI are initiated through excitation of the primary electron donor P700 positioned near the luminal side of the membrane-integral complex. Structurally, P700 consists of a chlorophyll a dimer (eC₁/eC₁*), whose mutually parallel dihydroporphyrin ring planes are aligned with the membrane normal. Upon excitation, P700* passes an electron to the primary electron acceptor A (probably eC₃ or eC₄; see below). Spectroscopically, the first electron acceptor has been identified as A₀, in all probability one (though possibly either) of the pair of Chl a monomers denoted eC₄ and eC₅ in the structural model of PSI (3, 4). This process occurs with a rate constant of about 5·10¹¹ s⁻¹ (5). The charge separation P700⁻ A₀ is spatially extended across the membrane by electron transfer from the radical A₀ to the next electron acceptor spectroscopically referred to as A₁; the rate constant is estimated to be 2·5·10¹⁰ s⁻¹ (for a review, see Ref. 5). A₁ is now generally agreed to be a phylloquinone (6, 7). Due to the difficulty of locating the small phylloquinone molecules in low resolution electron density maps and because of the stability of the radical state P700⁻ A₀, the position and orientation of A₁ relative to the PSI holocomplex has recently received increased attention, especially by improved EPR techniques. These have, *inter alia*, determined the distance between A₀ and P700⁻ to be −25.4 Å (8, 9, 10). A relative position for A₂ was derived through orientation-dependent pulsed EPR measurements on PSI single crystals (10). Geometrically, this position was found to correspond to QK, a single phylloquinone assigned to a well-defined pocket in the earlier electron density map (4). The assignment

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* The abbreviations used are: PSI, photosystem I; PsA, and PsB, large, central subunits of PSI, encoded by genes psaA and psaB; α and β, angles between vectors a and b; a, b-plane, crystallographic plane parallel to the membrane plane; C₆(AB), axis of pseudo-2-fold symmetry relating subunits PsAA and PsAB and also respective branches of the electron transfer system; Chl a, chlorophyll a; e-axis, crystallographic e-axis parallel to the membrane normal; eC₁ and eC₁*, luminal Chl a cofactors of the electron transfer system and its pseudosymmetric counterpart eC₁* and eC₁. eC₁, second and third pair of Chl a cofactors of the electron transfer system; eC₃ and eC₄, distances between named cofactor pairs (averaged value of pseudosymmetric branches); Qₐ and Qₐ*, phylloquinone cofactors of the electron transfer system; F₇, and F₉, preliminary x-ray structural model names for F₇ and F₉ (F₇ and F₉); P700, A₀, A₁, F₉, and F₉, spectroscopically identified cofactors of the electron transfer system of PSI as follows: primary electron donor (dimer of Chl a molecules), primary (single Chl a), secondary (phylloquinone), intermediate, and two terminal (Fe₄S₄ clusters) electron acceptors; m, n, and o and m', n', and o', α-helix nomenclature.
of this position, however, remained internally uncorroborated, since an expected pseudosymmetrically positioned second phylloquinone could not be identified at the time.

The three terminal cofactors of the electron transfer system are iron-sulfur centers, FX being closest to P700, followed by F1 and F2 (we retain this nomenclature, for the present, to emphasize the remaining structural ambiguity in their assignment to the known cofactors FA and FB, although see Refs. 11–13 as well as Ref. 14 for recent results correlating FA with F1 and FB with F2).

In the following, we describe an improved model of the electron transfer system of PSI based on the present electron density map at 4-Å resolution (14). This map reveals the position of the second phylloquinone molecule and allows the spatial positioning of all 11 cofactors of the electron transfer system of PSI. The positions and orientations of individual cofactors are discussed and compared with structural information derived from spectroscopic data.

**EXPERIMENTAL PROCEDURES**

**Calculation of an Improved Electron Density Map**—The phases for the electron density map presented here were derived using essentially the same data described previously (4), although a new native data set with a resolution of 3.5 Å and an additional mercury derivative data set have been included (14). Using the program SHARP (15) instead of the earlier combination VECREF/MLPHARE (16, 17) and including a total of five heavy atom derivative data sets, it was possible, by incorporating new minor sites, to derive a significantly improved heavy atom model. The program SOLOMON (16) has been employed in the solvent flattening procedure. Due to the low diffraction quality of heavy atom derivative crystals, experimentally obtained phase information is still limited to a resolution of 4 Å. Since no additional phase information at higher resolution could be achieved by phase extension using density modification techniques, the electron density map was calculated at a resolution of 4 Å. It reveals more detailed information on the polypeptide chain folding than previous maps as well as the complete cofactor set of PSI. For the detailed procedure and statistics for the determination of this electron density map, see Ref. 14.

**Model Building**—The previously reported model of the electron transfer system (3, 4) has been used as a basis for the present cofactor model. The Chl α head groups are visible as almost quadratically flat density pockets. The positions and orientations of the Chl α molecules are modeled by 4-fold symmetrical porphyrin moieties, since the present resolution does not permit their asymmetric features to be defined unambiguously. Similarly, the phylloquinone molecules are represented by their naphthalene moieties to interpret the corresponding elongated ellipsoidal electron density. Neither the phylloquinone side chains nor the oxygen atoms have been included in the model.

Chl α cofactors of the electron transfer system were placed into the electron density using the program O (18), and their positions were optimized using the real space refinement procedure as provided by this program.

**Distances between Cofactors and Associated Errors**—For Chl α molecules center-to-center distances were calculated between the central Mg2+ ions, while for iron-sulfur clusters and phylloquinones the centroid of the cluster and naphthalene model, respectively, have been used. Edge-to-edge distances of cofactors important for the kinetics of electron transfer were determined between the outer atoms of the porphyrin, naphthalene, and iron-sulfur cluster models, respectively. For iron-sulfur clusters, edge-to-edge distances have been determined between the iron and sulfur atoms of the clusters, as modeled. The estimated errors for center-to-center and edge-to-edge distances are on the order of ±1 and ±2 Å, respectively, the latter reflecting the larger uncertainties in the orientations of the planar cofactors within their molecular planes.

**RESULTS**

**Two Symmetrically Arranged Density Pockets Assigned to the Positions of the Phylloquinones**—In our previous x-ray structural model of PSI (4), only a tentative positional description of a single phylloquinone was included, assigned to an electron density pocket located between FX and eC3. The lack of a second, pseudosymmetrically positioned phylloquinone, however, prevented an internal corroboration of this identification. The new electron density map now reveals two such electron density structures symmetrically positioned on either side of the pseudo-2-fold rotation axis C2(AB) and located between eC3 and FX. These have been assigned to the phylloquinone electron acceptors QK and QK' (Fig. 1). The latter is equivalent to the position QK identified previously (4). Note that following our earlier convention of priming cofactors coordinated by primed α-helices, the position previously denoted QK will be renamed QK' (coordinated by α-helices m-n'), while the new second phylloquinone will be referred to as QK* (coordinated by m-n).

QK (QK') is situated slightly luminal of and close to the N terminus of α-helix n (n') and immediately adjacent to the loop connecting α-helices m and n (m' and n'). The corresponding electron density is clearly separated from that of the neighboring α-helices (Fig. 1). Facing away from the loop m-n (m'-n'), each phylloquinone is additionally delimited by the long loop n-o (n'-o') connecting the C-terminal end of n (n') to the stromal end of o (o').

In addition to QK and QK', a significantly more symmetrical arrangement of α-helices and connections on either side of the pseudo-2-fold axis C2(AB) is now apparent in its vicinity as compared with the previously published electron density map. Whereas the earlier model of the α-helix m almost passed through the position now assigned to QK*, the stromal end of m now has a comparable inclination relative to the membrane normal as its pseudosymmetric partner m'. The loops m-n (m'-n') connecting α-helix m (m') to the “surface” α-helix n (n') are similar in both shape and length (Fig. 2).

The electron densities of both QK and QK* are elongatedly ellipsoidal (Fig. 1). As a result, the long molecular axis of the naphthoquinone moiety may be identified with some confidence. However, the plane orientation as well as the quinone oxygen atoms remain indeterminate. As a result, the phylloquinone molecules have been modeled by their naphthalene backbone only. These naphthalene models were placed into the electron density optimizing their positions and the orientations of their long molecular axes. The molecular plane of QK was then rotated around the long axis to align the molecular plane with the vector eC3-QK to account for the observation that the carbonyl O-O-axis is approximately aligned with the...
vector $P700^{-}\Lambda_{1}'$ (19). Since the electron spin density is primarily located on either $eC_1$ or $eC_1'$ (20) (although which one remains to be clarified), the procedure was repeated to align the molecular plane of $Q_K$ with the vector $eC_1'^{-}Q_K$. Similarly, two plane orientations were obtained for $Q_K'$.

The long molecular axes of both $Q_K$ and $Q_K'$ are observed to be inclined by $13^{\circ}$ relative to the membrane plane (equivalent to the crystallographic $a,b$-plane). Projected onto the $a,b$-plane, the long molecular axis of $Q_K$ ($Q_K'$) describes an angle of $18^{\circ}$ ($60^{\circ}$) to the crystallographic $a$-axis. The axes of $Q_K$ and $Q_K'$ form an angle of $42^{\circ}$ with each other.

**The Iron-Sulfur Clusters**—The positions of the iron-sulfur clusters correspond to the highest electron density observed (21). $F_X$ was tentatively modeled by fitting a Fe$_4$S$_4$ cluster into the electron density. Contouring the electron density map at 11 S.D. above the mean density reveals a tetrahedrally distorted electron density structure associated with $F_X$ (Fig. 3). The most likely explanation is, that this tetrahedron is equivalent to the arrangement of the four iron atoms of the Fe$_4$S$_4$ cluster. Modeling a Fe$_4$S$_4$ cluster into this tetrahedral shape results in a good structural match, while the four sulfur atoms lie outside the contour, in agreement with their lower density of electrons. Interestingly, the derived orientation of $F_X$ upholds the 2-fold symmetry of $C_{2(AB)}$, a fact that had been assumed on grounds of symmetry yet had remained unsubstantiated. The observation that the $g_{xx}$ principal axis of the $g$ tensor of reduced $F_X$ is oriented perpendicular to the thylakoid membrane (22) now favors one of two alternative assignments of $g$ tensor axes to the distorted cubane structure of Fe$_4$S$_4$ clusters. According to EPR studies on Fe$_4$S$_4$ model compounds (23, 24), our structural model and the EPR results are in agreement with the assignment, where each of the three principal magnetic axes is normal to one of the mutually orthogonal faces of the distorted Fe$_4$S$_4$ cube (25).

The orientations of $F_1$ and $F_2$ have been inferred from the 2Fe$_4$S$_4$ ferredoxin structure from *Peptostreptococcus asaccharolyticus* (26) used as a model for PsaC (27). They are in agreement with those derived independently by EPR experiments on PSI single crystals (28). For $F_1$ and $F_2$, such tetragonally shaped density structures as observed in the case of $F_X$ are not evident as the electron density “outside” the membrane-integral region is less well defined.

**DISCUSSION**

**Overall Cofactor Arrangement**—The electron transfer system of PSI constitutes the innermost cylindrical core of the larger, membrane-integral photosynthetic reaction center complex. A set of 10 $\alpha$-helices, five from each of the two central subunits, PsaA and PsaB, tightly encloses the electron transfer...
of the electron transfer system have been identified, this
pseudosymmetry is seen to encompass the whole of the
membrane-integral region, extending from the pair \( \text{eC}_1/\text{eC}_1' \) near
the luminal side to \( \text{Q}_K/\text{Q}_K' \) near the stromal side (Fig. 2). The
iron-sulfur cluster \( \text{F}_X \) is located on the pseudo-2-fold axis
\( \text{C}_y(\text{AB}) \), completing the symmetrical arrangement at the
stromal edge of the membrane-integral subunits. Merely the two
stromal iron-sulfur clusters \( \text{F}_1 \) and \( \text{F}_2 (\text{F}_A \text{ and } \text{F}_B) \), coordinated by the
extrinsic subunit \( \text{PsaC} \), do not adhere to this 2-fold
symmetry.

In the direction parallel to the membrane normal, the
membrane-integral cofactors divide the membrane into four sections
of roughly comparable width, here denoted \( \text{eC}_1/\text{eC}_2, \text{eC}_2/\text{eC}_3, \text{eC}_3/\text{Q}_K, \) and \( \text{Q}_K/\text{F}_X \). The height difference for \( \text{eC}_1/\text{eC}_2, \text{eC}_2/\text{eC}_3, \text{eC}_3/\text{Q}_K, \) and \( \text{Q}_K/\text{F}_X \) amount to 5.9, 8.6, 7.8, and 8.8 Å,
respectively, while the total distance \( \text{eC}_1/F_X \) is 31.1 Å. This
corresponds to fractional distances of 0.19, 0.28, 0.25, and 0.28,
respectively (Fig. 4a).

Photovoltage measurements on oriented PSI thylakoid membranes
estimated values of fractional dielectrically weighted
transmembrane distances of 0.62 for \( \text{P700-A}_0 \) (compare with
\( \text{eC}_1/\text{eC}_2, 0.47), 0.16 for \( \text{A}_0/\text{A}_1 \) (compare with \( \text{eC}_2/\text{Q}_K, 0.25), \) and
0.22 for \( \text{A}_1/\text{F}_X \) (compare with \( \text{Q}_K/\text{F}_X, 0.28 \) (29, 30). These
relative distances, especially for the pair \( \text{P700-A}_0 \), do not corre-
spond to the x-ray structural model distances \( \text{eC}_1/\text{eC}_2 \), as
ewell as one might have expected. Because the distances \( \text{A}_0/\text{A}_1 \)
\( \text{eC}_2/\text{Q}_K \) and \( \text{A}_1/\text{F}_X \) (\( \text{Q}_K/\text{F}_X \)) are comparable (29), matching our
observations, the distance \( \text{P700-A}_0 (\text{eC}_1/\text{eC}_2) \) has clearly been
overestimated by the photovoltage measurements relative to the
other distances. Possibly, the fast rate of charge separation
results in a significant error for the distance \( \text{eC}_1/\text{eC}_2 \) (alterna-
tively, the dielectric constant around \( \text{P700} \) may differ substan-
tially from that nearer the middle of the membrane), giving rise
to the observed distortion.

*Intercofactor Distances from X-ray Structure and Spectroscopic Studies—Comparisons of structural and spectroscopic
data have recently been published based on models of PSI
derived at 4.5- and 4-Å resolution (4, 5). These studies, how-
ever, included none or, in the latter case, a single phylloqui-
none position designated \( \text{Q}_K \) (now renamed \( \text{Q}_K' \)). Here we will
include the latest structural results and compare these to the
available spectroscopic data.

The Moser-Dutton “ruler” (31) (an empirical first order rela-
tionship between electron transfer rates and shortest edge-to-
edge distances of the cofactors involved) provides a simple tool
to estimate the “optimal” electron transfer rates from struc-

![Diagram](image-url)

**Fig. 4. Schematic representations of the electron transfer system.**
- **a:** cofactor distribution along the membrane normal showing dis-
tances in Å and fractional distances. The observed center-to-center
distances (±1 Å) (b) and the edge-to-edge distances (±2 Å) (c) are
indicated. Except for the interplane distance between \( \text{eC}_1 \) and \( \text{eC}_1' \) (3.6 Å)
the values of the other edge-to-edge distances have been determined
with an accuracy of 0.5 Å. d, the individual distances and angles
between the cofactors \( \text{eC}_1, \text{eC}_1', \text{Q}_K, \) and \( \text{Q}_K' \) are shown. They corre-
spond to the center of the phylloquinones and are independent of the
phylloquinone plane orientations. Present distances and angles are
largely in agreement with those published previously (4). Note the
schematic nature of these diagrams; true distances are supplied but
may not be measured directly.

| Table 1 | The averaged edge-to-edge distances between the cofactor planes and the “optimal” electron transfer rates derived using the Moser-Dutton relationship, \( \log k_{ET} = 15 - 0.66R - 3.1|\Delta G^*| + 0.77|\lambda| (31). \)
| --- | --- |
| Structural data | Selected spectroscopic data |
| Distance from \( \to \) | Edge-to-edge distance (±2 Å) | Calculated optimal electron transfer rates, \( k_{ET} (\Delta G^* = \lambda) \) | Electron transfer | Edge-to-edge distance | Electron transfer rates, \( k_{ET} \) |
| \( \text{eC}_1 \to \text{eC}_2 \) | 4 | 4.0 \( \times \) \( 10^{12} \) | \( \text{P700} \to \text{A}_0 \) | 5 \( \times \) \( 10^{13} \) (5)* |
| \( \text{eC}_1 \to \text{eC}_3 \) | 13.3 | 1.0 \( \times \) \( 10^{7} \) | \( \text{P700} \leftarrow \text{A}_1 \) | 4 \( \times \) \( 10^{7} \) (5)* |
| \( \text{eC}_2 \to \text{Q}_K \) | 20.5 | 5.0 \( \times \) \( 10^{9} \) | \( \text{A}_0 \to \text{A}_1 \) | \( \pm 7.8 \) (33) |
| \( \text{eC}_3 \to \text{F}_X \) | 26.5 | 1.3 \( \times \) \( 10^{10} \) | (2-5) \( \times \) \( 10^{10} \) (5)* |
| \( \text{eC}_3 \to \text{Q}_K \) | 5 | 1.0 \( \times \) \( 10^{12} \) | \( \text{A}_1 \to \text{F}_X \) | 10.7 (34) |
| \( \text{Q}_K \to \text{F}_X \) | 11.3 | 1.7 \( \times \) \( 10^{9} \) | 1.5 \( \times \) \( 10^{9} \) (34) |
| \( \text{F}_X \to \text{F}_1 \) | 12 | 6.3 \( \times \) \( 10^{7} \) | \( \text{F}_1 \to \text{F}_2 \) | 1.0 \( \times \) \( 10^{7} \) |
| \( \text{F}_1 \to \text{F}_2 \) | 20 | 4.0 \( \times \) \( 10^{8} \) |

* See Ref. 5 for original publications.
* Charge recombination rate.
* The reaction free energy is presumably not equivalent to the reorganization energy as simplifyingly assumed for the calculation of electron transfer rates in this table.
tural data, the optimal electron transfer rate being achieved when the sum of the standard reaction free energy and reorganization energy is essentially zero (32). In Table I, the edge-to-edge distances and the optimal (i.e. fastest theoretically possible) electron transfer rates derived, using the above relationship, are listed.

Chlorophyll a Cofactors—The Chl a molecules, eC1, eC1’, eC2, eC2’, eC3, and eC3’ constitute the luminal half of the electron transfer system. eC1 and eC1’ have been identified as structural components of the spectroscopically identified primary electron donor P700; eC2 and eC2’ are referred to as the accessory chlorophylls; while either or both of eC3 and eC3’ have been assigned to the spectroscopically identified primary electron acceptor A∗.

As noted (4, 5), the edge-to-edge distance between eC1 and eC2 of 13.3 Å is too long to be compatible with the electronic transfer rate of 5×10¹¹ s⁻¹ (for a review, see Ref. 5) determined for the primary electron transfer step (see Table I, Fig. 4c). It therefore seems likely that neither eC1 nor eC1’ (the spectroscopically identified electron acceptor A∗), but one or both of eC2 and eC2’, represent an additional intermediate (i.e. true primary electron acceptor) with a calculated optimal electron transfer rate from eC1 to eC2 of 4×10¹² s⁻¹ and eC2 to eC3 of 1×10¹² s⁻¹ (see Table I).

The Phyloquinone Electron Acceptors—The average center-to-center distance between QK and the neighboring cofactor eC3 amounts to 8.7 Å. Combining data from pulsed EPR experiments on the position of the quinone cofactor (relative to P700 and the x-ray structural model of PSI yielded a comparable center-to-center distance estimate of 7.5 ± 2 Å for eC3-QK (10).

The center-to-center distance between QK and FX has similarly been estimated to be 14 ± 2 Å by EPR measurements (10), matching that of the x-ray structural model (QK/QK’-FX = 14.3 ± 1/14.1 ± 1 Å (Fig. 4b)). Although the orientation of the molecular plane of QK about the naphthalene long axis could not be determined from the electron density map, we determined the edge-to-edge distances to the surrounding cofactors. Compared with the overall errors estimated for edge-to-edge distances (±2 Å), the distances observed for the two QK plane orientations modeled prove insignificant.

The averaged edge-to-edge distance eC1-QK of 4.8 ± 2 Å is somewhat shorter than the value of 7.8 Å estimated from pico-nanosecond laser spectroscopy (33) (Table I). The difference between these values is possibly due to the inequivalence of the reaction free energy and reorganization energy, causing the distance to be overestimated (33). The averaged edge-to-edge distance between QK and FX is 11.3 Å ± 2 Å, which agrees well with the 10.7 Å suggested previously (34) (Table I).

The discrepancy between the electron transfer rate derived from the edge-to-edge distance eC1-QK and those rates reported for the charge recombination reaction P700⁺-A∗→P700A∗ proves to be slightly more problematic; the latter is roughly 4×10¹² s⁻¹ (5) (Table I). According to the Moser-Dutton approximation (31), the optimal (i.e. fastest possible) transfer rate for a direct recombination through the distance eC1-QK (20.5 Å) would be in the range of 5.0×10¹² s⁻¹. The reason for the observed rates being faster than that calculated from the corresponding edge-to-edge distance for this pair of cofactors is unclear, although an intermediate step in recombination could provide an explanation of this difference.

Correlation of A∗ with QK or QK’—The identification of two phylloquinones and their introduction to the x-ray structural model gives new impetus to the question of which one of QK or QK’ corresponds to the spectroscopically identified cofactor A∗.

To analyze the current possibilities, we derived two orientational models for each phylloquinone (see “Results”). The orientation and position of each of these models (two for each QK and QK’) are quantified by the parameters shown in Fig. 5.

The distance between P700⁺ and A∗ has been placed at 25.4 ± 0.3 Å (8, 9). The center-to-center distances of all four combinations (eC1-QK, eC1’-QK, eC1-QK’, and eC1’-QK’) are compatible with the EPR data (Table II, Fig. 4d).

The inclination of P700⁺-A∗ relative to the membrane normal (e-axis) is 27 ± 5° (10, 35). The corresponding values for eC1-QK, eC1’-QK, eC1-QK’, and eC1’-QK’ are 23, 28, 31, and 29 ± 2°, respectively (Table II, Fig. 4d; see also a in Fig. 5). A unique assignment of P700⁺-A∗ is thus not obtained, although eC1-QK and eC1’-QK give the closest agreement.
**Table II**

| Parameter | EPR (A₁) | X-ray crystallography | Qₓ | Qₓ’ |
|-----------|----------|------------------------|----|-----|
| ε        | (long axis); a, b-plane | 13 ± 5° | 13 ± 5° |
| μ        | (projection of the long axis onto the a, b-plane; a-axis) | 18 ± 5° | 0 ± 5° |
| Length of P700⁻⁻-A7 | 25.4 ± 0.3 Å (8, 9) | 24.4 ± 1 Å | 25.5 ± 1 Å | 25.7 ± 1 Å | 25.2 ± 1 Å |
| ω        | (projection of P700⁻⁻-A7 onto the a, b-plane; a-axis) | 27 ± 5° (10) | 22 ± 3° (20/25) | 28 ± 3° (27/29) | 31 ± 3° (3/31) | 29 ± 3° (27/30) |
| φ        | (O-O-axis; P700⁻⁻-A7) | 0 ± 1° (19) | 15 ± 1° (14/17) | 14 ± 1° (14/15) | 15 ± 1° (12/18) | 1 ± 1° (2/24) |
| β        | (O-O-axis; c-axis) | 27 ± 10° (35) | 27 ± 10° | 17 ± 10° | 35 ± 10° | 28 ± 10° |
| δ        | (molecular plane; a, b-plane) | 76 ± 10° (35) | 56 ± 1° | 59 ± 1° | 50 ± 10° | 52 ± 10° |
| γ        | (C₇–C₅methyl; c-axis) | 35 ± 20° (36) | 49 ± 1° | 45 ± 1° | 53 ± 10° | 51 ± 10° |
| η        | (long axis; P700⁻⁻-A7; both a, b-plane) | 30 ± 5° (26/34) | 68 ± 5° (62/73) | 81 ± 5° (76/87) | 68 ± 5° (62/73) |

**a** "Long axis" is equivalent to the phylloquinone long molecular axis.

**b** The term "a-axis" not only describes the true crystallographic a-axis but also the b-axis, as well as the a+b-axis (60° from either a- or b-axis) including their negative directions, since these are indistinguishable in the EPR data.

**c** Values in parentheses indicate the two extreme cases where the spin density of A₇* is located on either one of the two naphthoquinone rings. Especially in projection onto the a, b-plane these may differ substantially from those obtained using the molecular centroids (see dotted lines in Fig. 5).

**d** "Molecular plane" implies molecular plane of the phylloquinone molecules.

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ω—the angle between the projection of P700⁻⁻-A7 onto the a, b-plane and the a-axis (ω in Fig. 5c) is put at 0 ± 10° by EPR simulations (10). It should be noted that because of the inherent D₃ symmetry of these EPR techniques, the above values do not only hold for the crystallographic a-axis but also for the equivalent directions described by the vectors b and (a + b). In the following, the term "a-axis" therefore includes the true crystallographic a-axis, as well as its repetitions at 60° intervals in the a, b-plane. The corresponding values for ω derived from the x-ray structural model are 12° (eC₁₁-QK), 10° (eC₁⁻⁻-QK), 21° (eC₁⁻⁻⁻⁻-QK), and 5° (eC₁⁻⁻⁻⁻⁻⁻⁻⁻-QK). Here eC₁₁⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻˓→
Electron Transfer System of Photosystem I

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