

Figure S1. UV-Vis transmittance of a) U-360, b) Y-50 and c) glass filters used for filtering the illuminated white light.

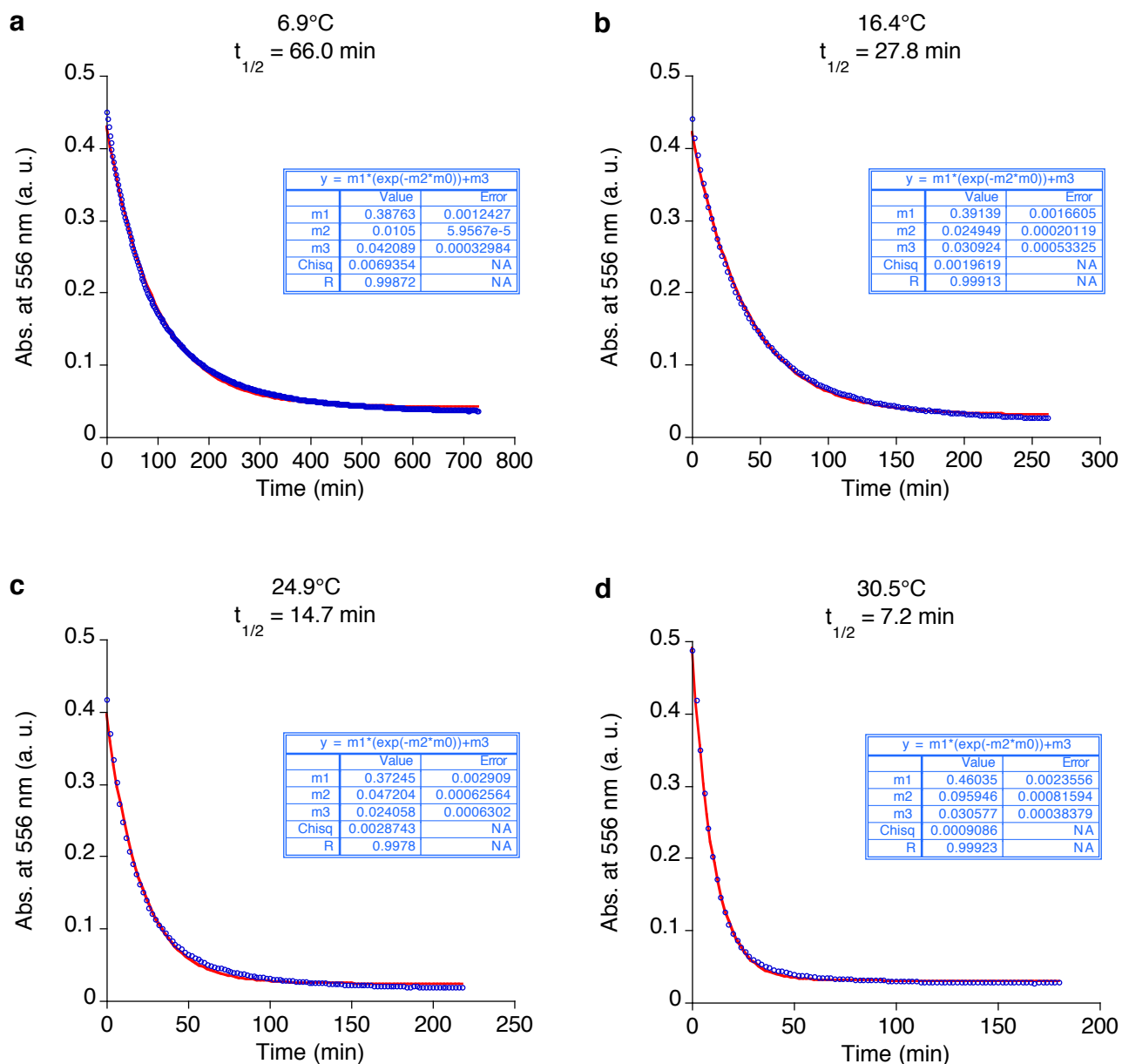


Figure S2. Half-lives of R111K:R132L:Y134F:T54V:R59W/retinal complex after white light irradiation using UV filter for 1 min at varying temperatures a) 6.9 °C, b) 16.4 °C, c) 24.9 °C, d) 30.5 °C. The half-lives were determined through fitting the data to an exponential decay (pseudo first order) shown in Eq. (1) of the main text experimental procedure. For a plot showing the overlay of the kinetic data, see Figure 3a in the main text.

Calculations of Thermodynamic Parameters

Table S1 tabulates the rate constant (k) of reactions at different temperatures.

Table S1. Summary of kinetic data obtained with varying temperature.

T (K)	k (min ⁻¹)
280.05	0.0105
289.55	0.0249
298.05	0.0472
303.65	0.0959

Arrhenius Plot

An Arrhenius plot was obtained by plotting $\ln(k)$ versus $1/T$ (Figure S3).

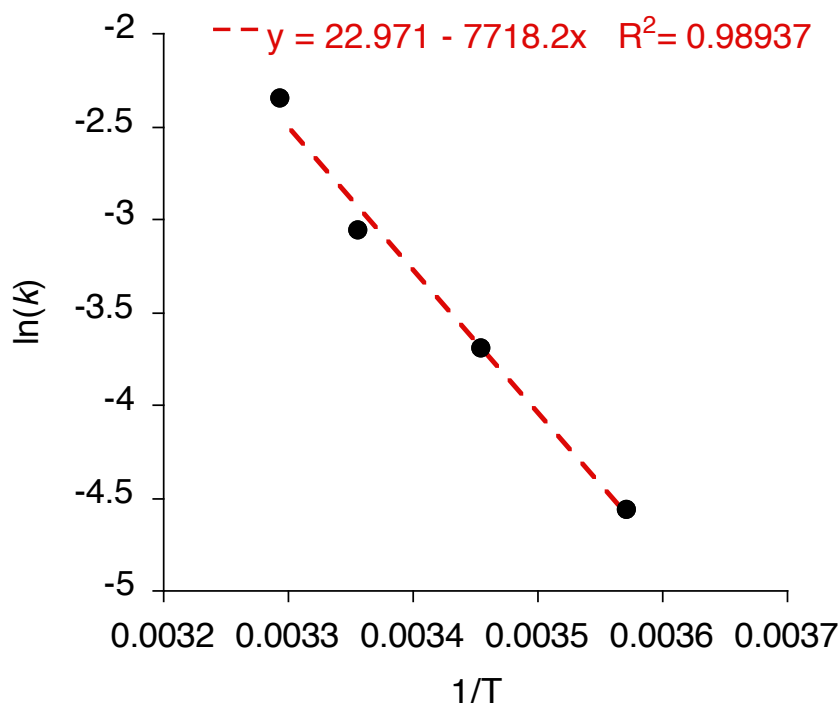


Figure S3. Arrhenius plot showing the effect of temperature on the rate constant k .

The Arrhenius equation (Eq. (4)) can be rearranged to solve for a linear relationship between $\ln(k)$ and $1/T$ (eq 4).

$$k = Ae^{-E_a/RT} \quad \text{Eq. (4)}$$

$$\ln(k) = \left(\frac{-E_a}{R}\right)\left(\frac{1}{T}\right) + \ln(A) \quad \text{Eq. (5)}$$

where k is the reaction rate constant, E_a is the activation energy, A is the preexponential factor, T is the absolute temperature and R is the gas constant.

The slope and y-intercept from the linear formula obtained in Figure S3 can be fitted to Eq. (5), to solve for the activation energy (E_a) and the preexponential factor (A), respectively:

$$\frac{-E_a}{R} = -7718.2 \quad \rightarrow \quad E_a = 64 \text{ kJ mol}^{-1} = 15.4 \text{ kcal mol}^{-1}$$

$$\ln(A) = 22.971 \quad \rightarrow \quad A = 9.5 \times 10^9$$

Eyring Plot

An Eyring plot was obtained by plotting $\ln(k/T)$ versus $1/T$ (Figure S4)

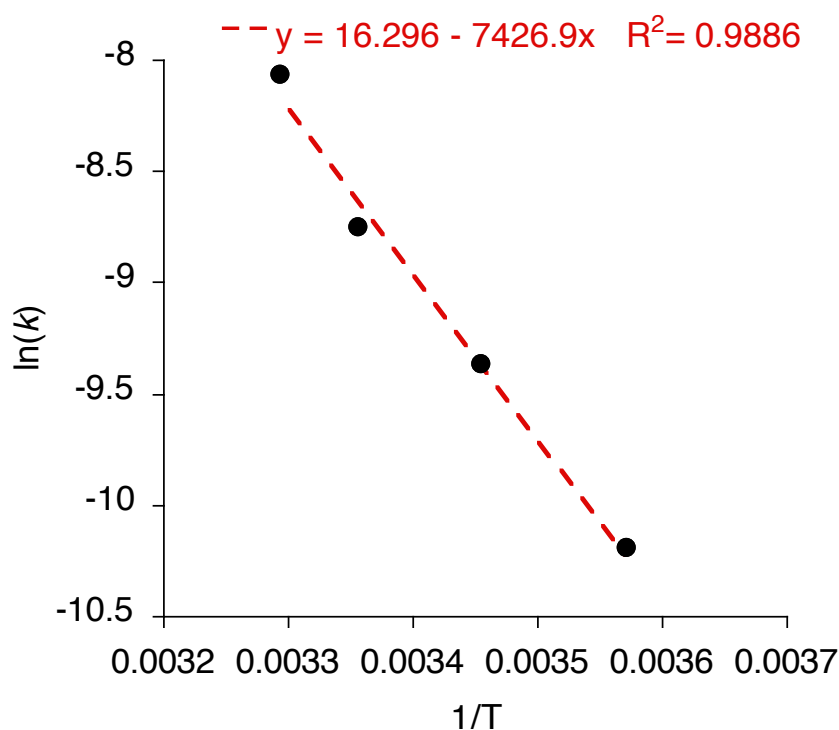


Figure S4. Eyring plot showing the effect of temperature on the rate constant k .

The Eyring equation (Eq. (6)) can be rearranged to the linear form (Eq. (7)).

$$k = \frac{k_B T}{h} e^{-\frac{\Delta G^*}{RT}} \quad \text{Eq. (6)}$$

$$\ln \frac{k}{T} = \frac{-\Delta H^*}{R} \times \frac{1}{T} + \ln \frac{k_B}{h} + \frac{\Delta S^*}{R} \quad \text{Eq. (7)}$$

where k is the reaction rate constant, E_a is the activation energy, T is the absolute temperature, ΔH^* is the enthalpy of activation, R is the gas constant, k_B is the Boltzmann constant, h is Planck's constant and ΔS^* is the entropy of activation.

The slope and y-intercept from the linear formula obtained in Figure S4 can be fitted to Eq. (7), to solve for the enthalpy of activation (ΔH^*) and the entropy of activation (ΔS^*), respectively:

$$\frac{-\Delta H^*}{R} = -7426.9 \quad \rightarrow \quad \Delta H^* = 62 \text{ kJ mol}^{-1} = 14.8 \text{ kcal mol}^{-1}$$

$$\ln \frac{k_B}{h} + \frac{\Delta S^*}{R} = 16.296 \quad \rightarrow \quad \Delta S^* = 62 \text{ J mol}^{-1} = 14.8 \text{ cal mol}^{-1} \text{ K}^{-1}$$

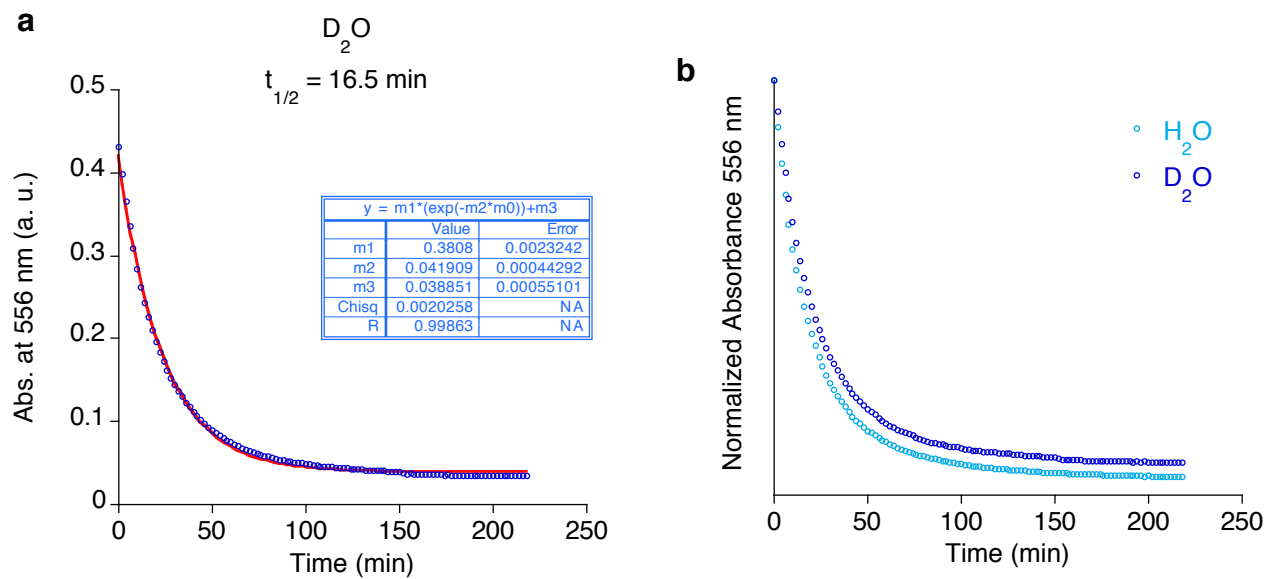


Figure S5. Half-lives of R111K:R132L:Y134F:T54V:R59W/retinal complex after white light irradiation using UV band-pass filter for 1 min a) D_2O b) D_2O overlaid with H_2O from Figure S2c. The half-lives were determined through fitting the data to an exponential decay (pseudo first order) shown in Eq. (1) of the main text experimental procedure.

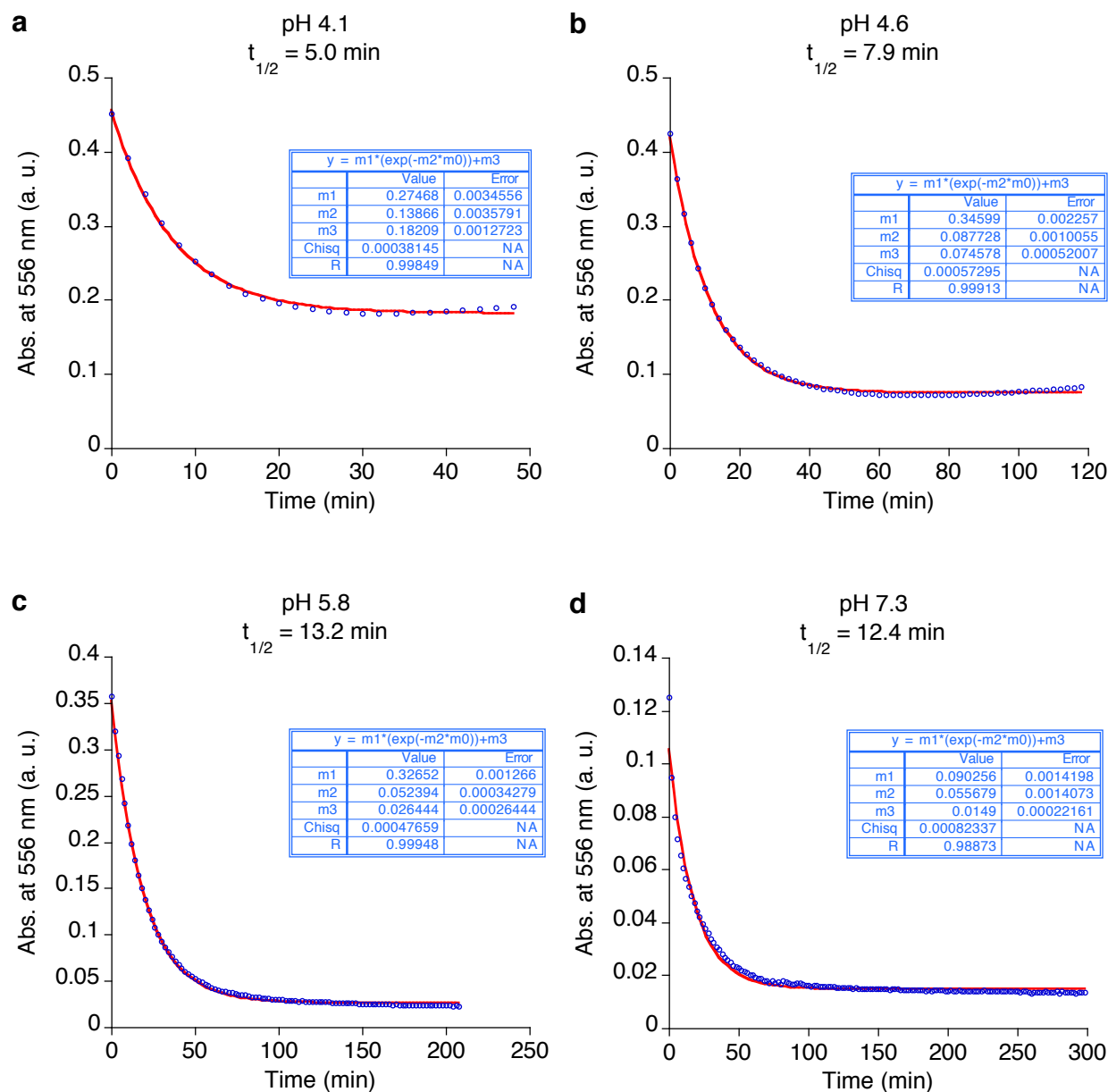


Figure S6. Half-lives of R111K:R132L:Y134F:T54V:R59W/retinal complex after white light irradiation using UV band-pass filter for 1 min at varying pH values a) pH 4.1, b) pH 4.6, c) pH 5.8, d) pH 7.3. The half-lives were determined through fitting the data to an exponential decay (pseudo first order) shown in Eq. (1) of the main text experimental procedure. For the kinetic plot at pH 5.2, see Figure S2c. For a plot of the rate versus pH see Figure 4a in the main text.

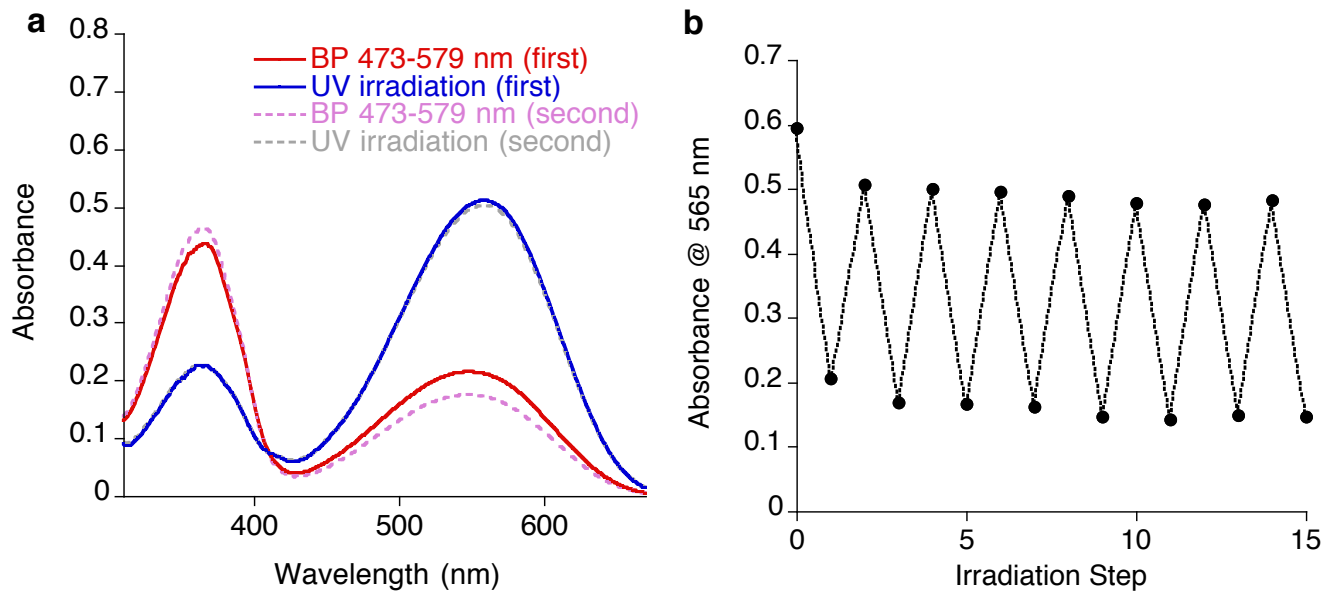


Figure S7. a) UV-vis traces after iterative UV and visible light (BP 473-579 nm) irradiation of the Q108K:K40L:T51V:R58F-hCRBPII/retinal complex; b) The absorbance at 565 nm measured after 15 cycles of alternating UV and visible light irradiation.

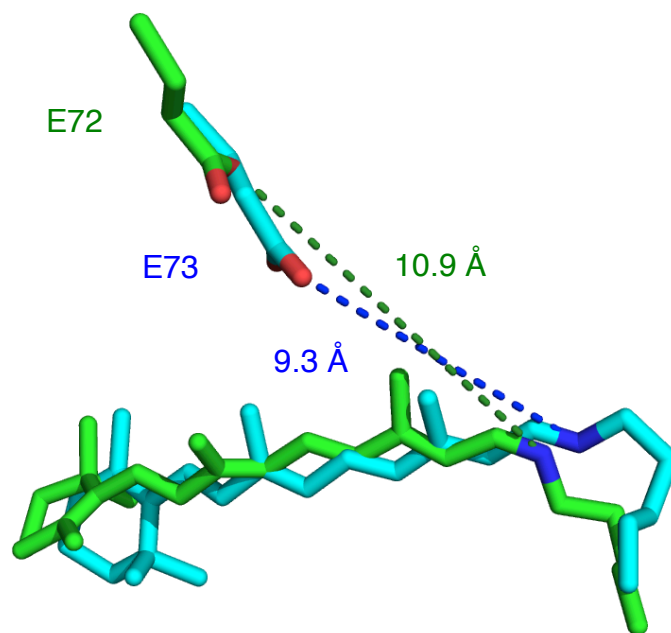


Figure S8. Overlay of R111K:R132L:Y134F:T54V:R59W-CRABP II/retinal (cyan) and Q108K:K40L:T51V:R58F-hCRBP II/retinal (green) crystal structures. In CRABP II, the distance from E73 to the iminium nitrogen is 9.3 Å. In hCRBP II, the distance from E72 to the iminium nitrogen is 10.9 Å.