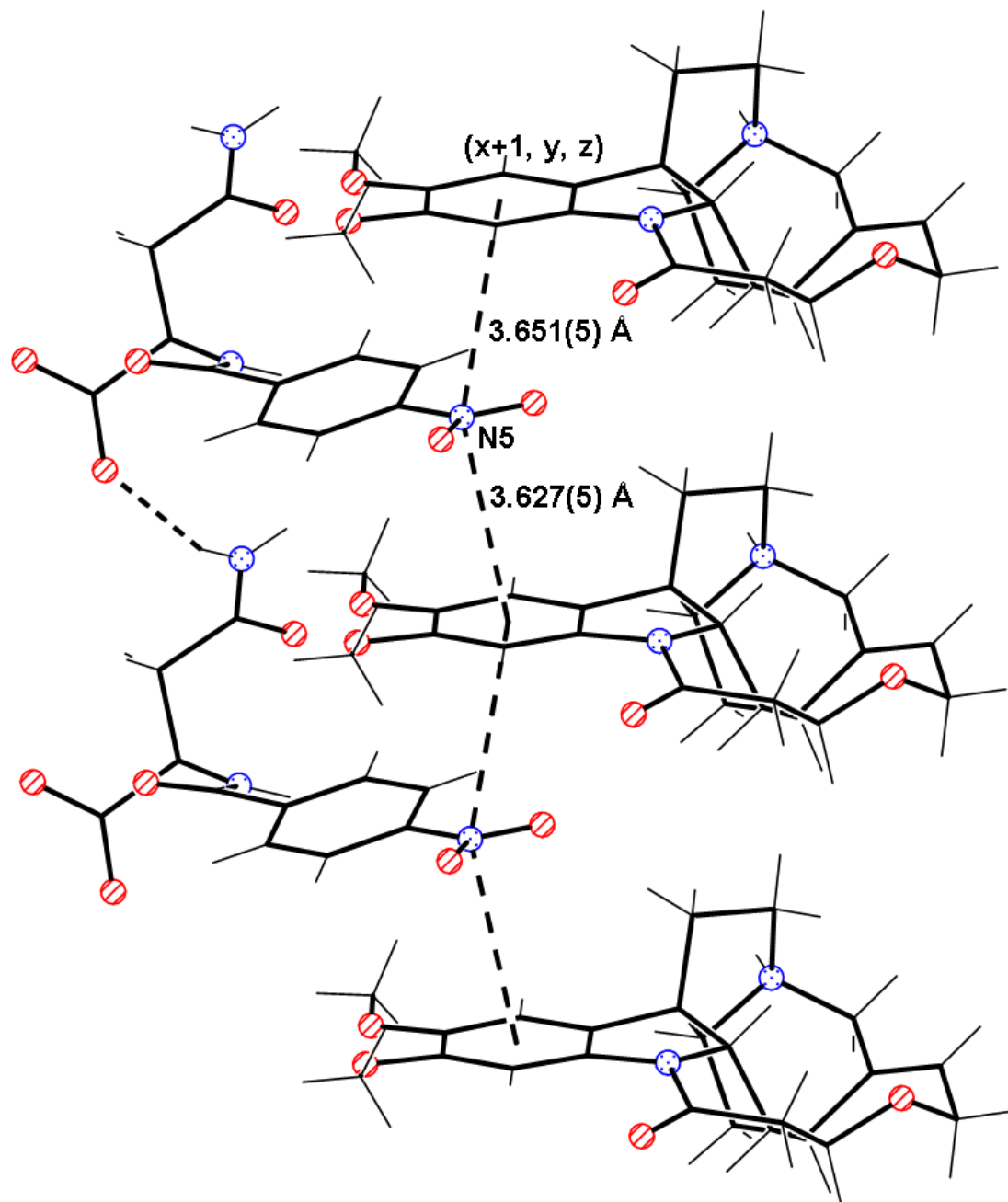


Fig. S1 Nitro... π stacking interactions in 1. Angle between plane of arene ring of cations and nitro group of anions (with approximate esd) is equal to $5.19(9)^\circ$, and slippage of the nitro... π and nitro... $\pi(x+1, y, z)$ interactions is equal to 0.69 and 0.83 Å, respectively.



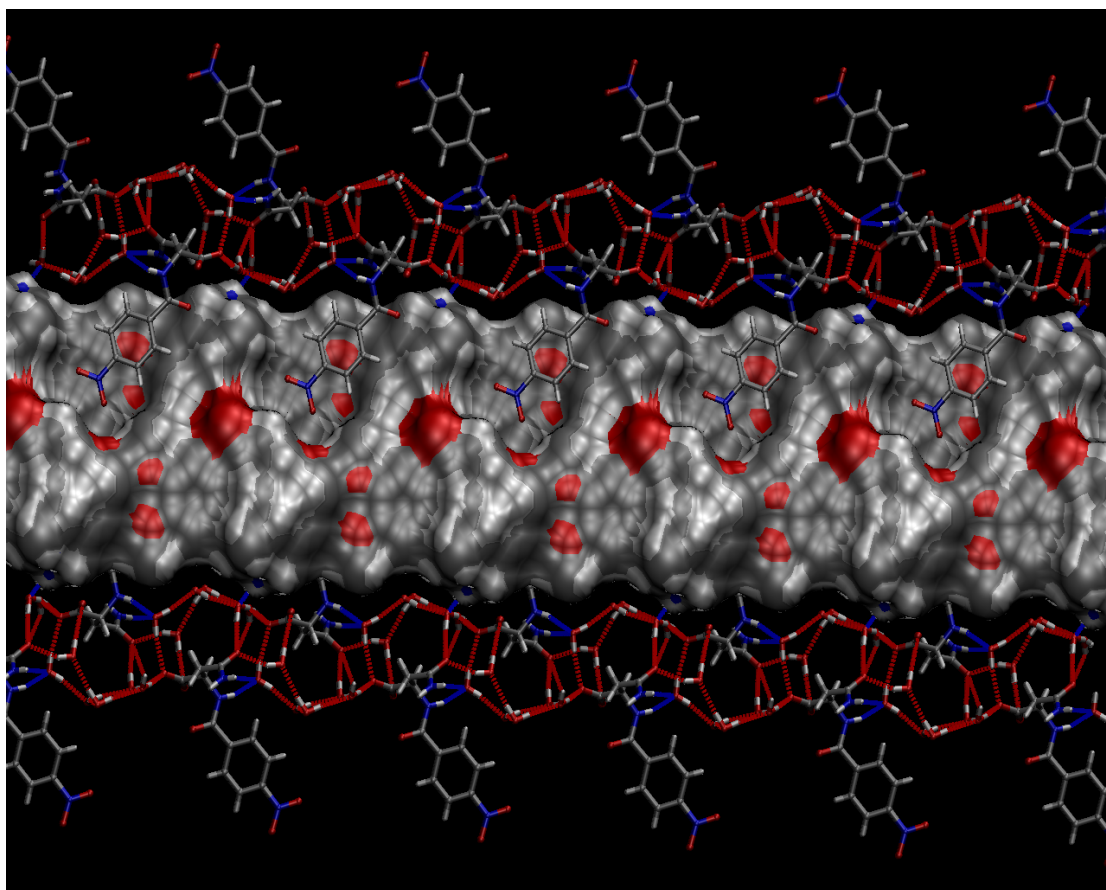


Fig.
S1a

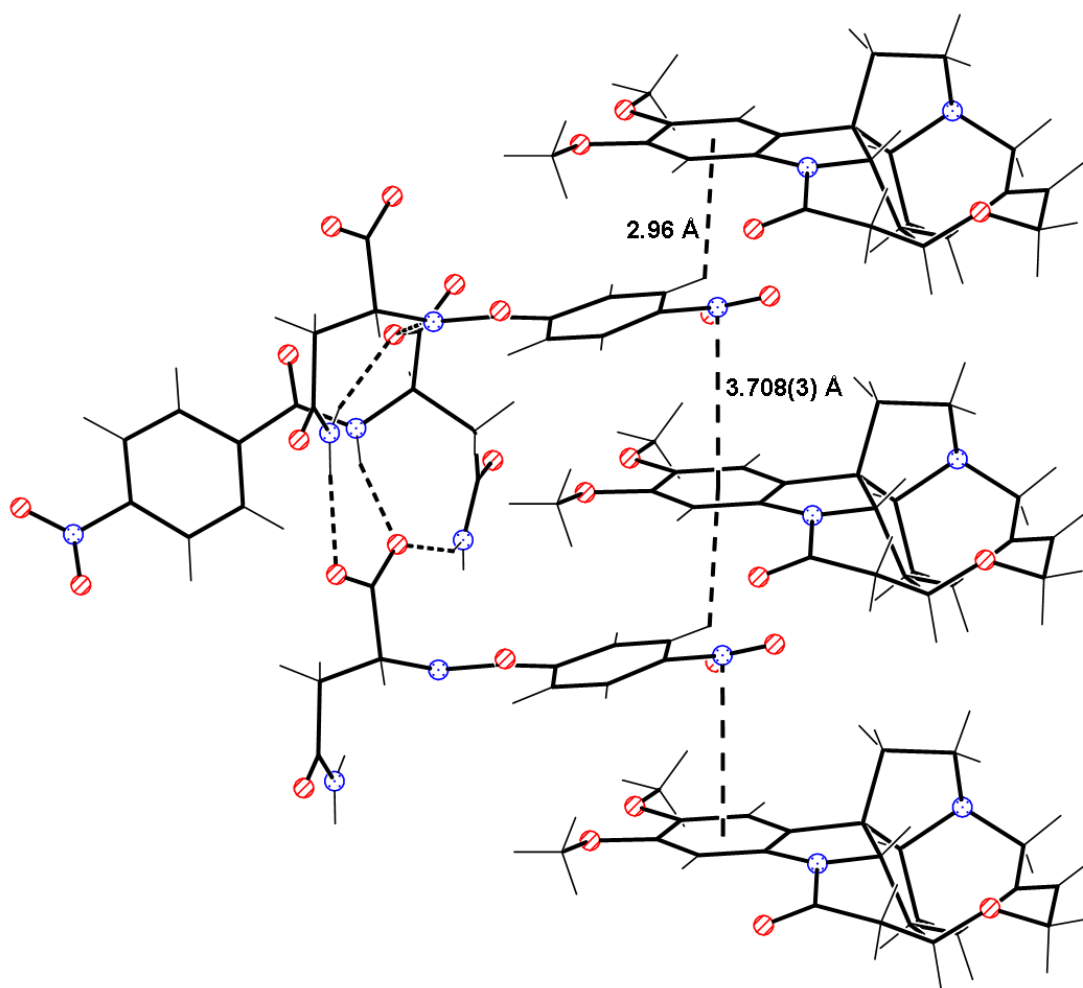


Fig. S2 C-H...O hydrogen bonds and nitro...O stacking interactions in 1a. Angle between plane of arene ring of cations and nitro group of anions (with approximate esd) is equal to $24.66(16)^\circ$, and slippage of the nitro...O ($1.5-x, -y+1, -0.5+z$) interactions is equal to $0.91 \text{ \AA}$. Geometry of the C-H...O hydrogen bond (Cp1 – centroid of brucinium arene ring): $\text{C31-H31} = 0.95 \text{ \AA}$, $\text{H31}\cdots\text{Cp1}(0.5-x, -y+1, -0.5+z) = 2.96 \text{ \AA}$, $\text{C31}\cdots\text{Cp1}(0.5-x, -y+1, -0.5+z) = 3.500(3) \text{ \AA}$, $\text{C31-H31}\cdots\text{Cp1}(0.5-x, -y+1, -0.5+z) = 118^\circ$, offset = $0.29 \text{ \AA}$.

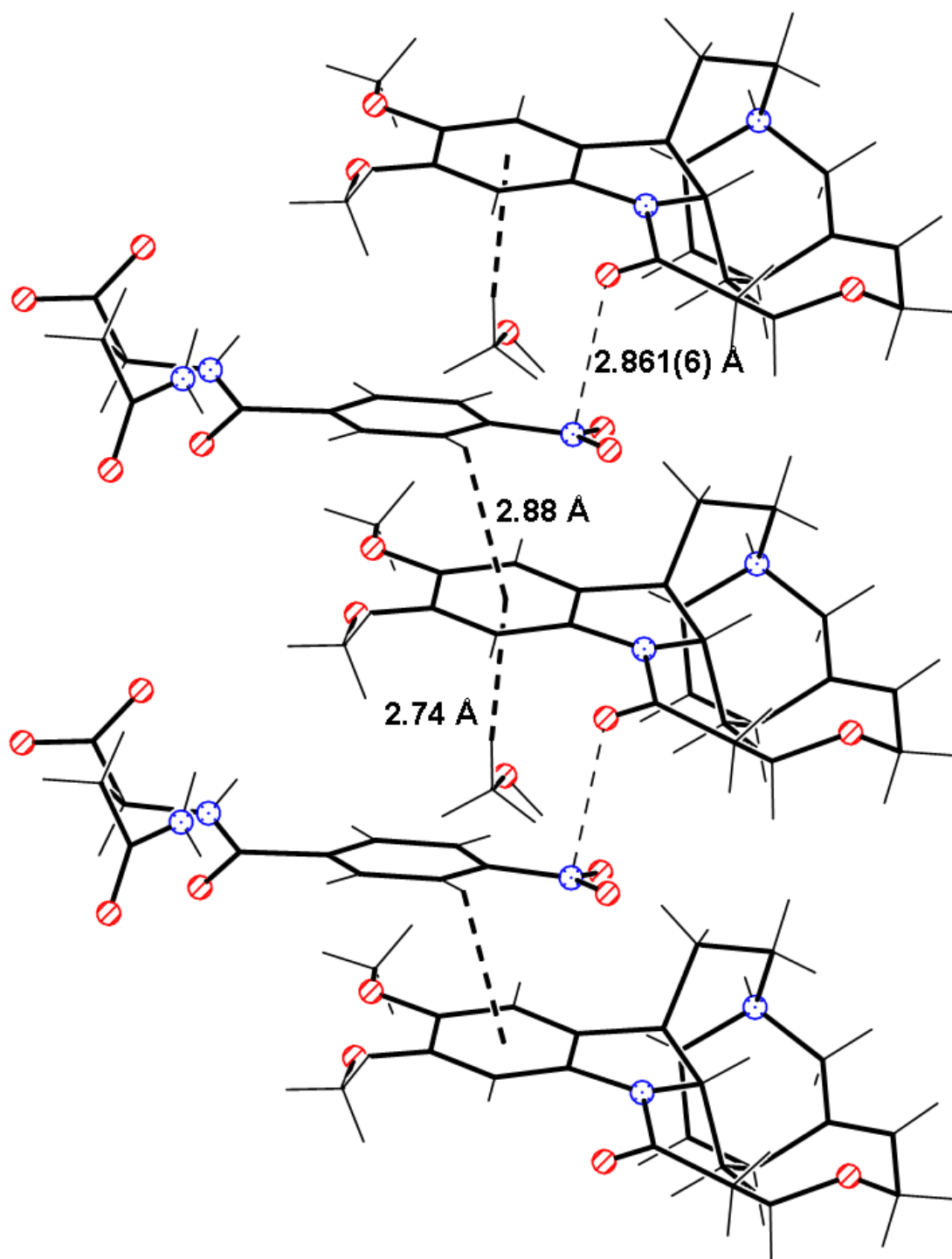


Fig. S3 C-H...O hydrogen bonds and N...O interactions in 2. Geometry of the C-H...O hydrogen bond (Cp1 – centroid of brucinium arene ring): C35-H35 = 0.98 Å, H35A...Cp1 = 2.74 Å, C31...Cp1 = 3.712(5) Å, C35-H35A...Cp1 = 174 °, offset = 0.23 Å; C31-H31 = 0.95 Å, H31...Cp1(1.5-x, 1-y, 0.5+z) = 2.88 Å, C31...Cp1(1.5-x, 1-y, 0.5+z) = 3.558(4) Å, C31-H31...Cp1(1.5-x, 1-y, 0.5+z) = 129 °, offset = 0.91