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Charge-transfer chemistry of two corticosteroids used adjunctively to treat COVID-19. Part II: The CT reaction of hydrocortisone and dexamethasone donors with TCNQ and fluoranil acceptors in five organic solvents

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ABSTRACT

Hydrocortisone (termed as D1) and dexamethasone (termed as D2) are corticosteroids currently used to treat COVID-19. COVID-19 is a disease caused by severe acute respiratory syndrome coronavirus 2 (SARS-CoV-2). Exploring additional chemical properties of drugs used in the treatment protocols for COVID-19 could help scientists alike improve these treatment protocols and potentially even the vaccines (i.e., Janssen, Moderna, AstraZeneca, Pfizer-BioNTech). In this work, the charge-transfer (CT) properties of these two corticosteroids (D1 and D2) with two universal acceptors: 7,8,8-tetracyanoquinodimethane (termed as TCNQ) and fluoranil (termed as TFQ) in five different solvents were investigated. The examined solvents were MeOH, EtOH, MeCN, CH2Cl2, and CHCl3. The CT interactions formed stable corticosteroid CT complexes in all examined solvents. Several spectroscopic parameters were derived, and the oscillator strength (f) and transition dipole moment (l) values revealed that the interaction between the investigated corticosteroids with TCNQ acceptor is much stronger than their interaction with TFQ acceptor. The CT interactions were proposed to process via n→π⁎ transition.

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1. Introduction

On December 9, 2019, a novel coronavirus (severe acute respiratory syndrome coronavirus 2, SARS-CoV-2) originated from a seafood market in Wuhan, China, rapidly becoming a destabilizing global pandemic. By early March 2020, after the SARS-CoV-2 outbreak had affected millions worldwide, the World Health Organization (WHO) termed the acute respiratory syndrome resulting from SARS-CoV-2 infection the COVID-19 (COVID-19) and declared it a pandemic [1–3], become the biggest outbreak that the world ever seen [4]. COVID-19 has killed more than 6.15 million and infected more than 490 million people worldwide (as of April 1, 2022) [5]. Several pharmacological approaches have been implemented based on previous evidence from prior outbreaks of respiratory-targeting viruses, such as SARS-CoV in China in 2003 and the MERS-CoV in the Middle East in 2012 [6,7]. These therapeutic approaches include corticosteroids, tocilizumab, azithromycin, lopinavir/ritonavir, remdesivir, chloroquine, and hydroxychloroquine. For more than 70 years, corticosteroids have been used in the treatment of inflammatory diseases, and oral infections due to their strong immunomodulatory and anti-inflammatory properties; in general, corticosteroids modulate the immune response to treat a wide variety of diseases by preventing and attenuating inflammation [8,9]. Corticosteroids are widely used adjunctively to treat critically ill patients with COVID-19 because they reduce inflammation-induced lung injury by suppressing lung inflammation [10–14]. Corticosteroids decrease patients’ dependency on mechanical ventilation, the duration of shock on circulatory support, the length of intensive care unit (ICU) stays, and potentially even mortality.
nadiene-3,20-dione (dexamethasone), their chemical structures are shown in Fig. 1, are the most widely used corticosteroids in the treatment of COVID-19. Dexamethasone and hydrocortisone possess strong anti-inflammatory properties and treat severe skin allergies and inflammation, but dexamethasone has potent anti-inflammatory effects more than hydrocortisone by 25–50 times [15,16]. Because of that, dexamethasone is well suited for short-term use in acute and severe inflammatory cases and is also used to treat aphthous stomatitis, vesicular stomatitis, and ulcers. It inhibits the production of new immune cells and the formation of prostaglandins (pro-inflammatory substances), thereby suppressing the amplification of immune reactions [17–19].

Charge transfer (CT) or donor-acceptor complexations are interactions that involve transferring an electronically charged particle between two molecules; the one that donates the charge is commonly known as the electron-donating (donor; D) molecule, whereas the one that accepts the charge is commonly known as the electron-accepting (acceptor; A) molecule. The transferring could be symbolized as (D → A), and the generated complex by this interaction could be formulated as [D+ A ] [20–27]. After Robert Mul-liken introduced the concept of CT interaction in 1969, Roy Foster widely disseminated it, and since then, it has become well established that CT interactions involve the formation of a weak bond combined with a great color change. The strong color changes used to identify the resultant CT complex reflect a change in the UV/Vis spectrum of D and/or A molecules appearing in the form of either a new absorption band that did not exist in the spectra of the D and A molecules or increasing of the intensity of the already existing UV/Vis bands.

CT interactions researchers noted that the generated products possess unique chemical, physical, and biological properties via this type of interaction. Beneficiations of CT interactions are not limited to basic sciences (biology, biochemistry, chemistry, physics) but extended to applied sciences (medicine, pharmacology, technology, industry, material science, engineering) [21,28–86]. In the past years, we have been interested in examining the CT behavior of numerous biologically active donor molecules by reacting them with different organic and inorganic accepting molecules in different media [87–121]. Since the onset of the SARS-CoV-2 pandemic, we shifted our focus from biologically active donor molecules to the CT properties of the pharmacological agents used to combat COVID-19 and their modifiability. We think obtaining new insights into the CT behavior of active compounds used in the treatments for COVID-19 will provide insight into the mechanisms underlying their effective properties and can help scientists alike to optimize and improve these treatment protocols and potentially even the vaccines (Janssen, Moderna, AstraZeneca, Pfizer-BioNTech). In a four-part work, we pioneered this new research effort with a comprehensive investigation into the CT chemistry of azithromycin, an antibiotic widely used in the treatment of COVID-19 [34–37].

As a continuation of these works, our newest series aims to furnish a big-picture perspective on the CT property of hydrocortisone and dexamethasone, corticosteroids widely used in the treatment of COVID-19. In part I [122], we described the CT interactions of these two corticosteroids with the 2,3-dichloro-5,6-dicyano-p-benzoquinone acceptor. In the current part of the work (Part II), we described the CT interactions of hydrocortisone and dexamethasone with two new accepting-molecules, 7,7,8,8-tetracyanoquinodimethane (termed as TCNQ) and fluoranil (termed as TFQ) (Fig. 2) in five organic solvents.

2. Experimental

2.1. Reagents and solvents

The used solvents in this study: MeOH, EtOH, MeCN, CH2Cl2, and CHCl3 were spectroscopic-grade solvents and obtained from Fluka (Lausanne, Switzerland). The investigated organic acceptors supplied by the Merck KGaA (Darmstadt, Germany) were 7,7,8,8-tetracyanoquinodimethane (TCNQ) and fluoranil (TFQ). The examined donors obtained from Sigma-Aldrich (Saint Louis, MO, USA) were hydrocortisone (abbreviated here as D1) and hydrocortisone (abbreviated here as D2). All the donors and acceptors were obtained from the commercial sources at the highest purity available, which were ≥ 98 % HPLC for D1, 99 % HPLC for D2, 98 % for TCNQ, and 97 % for TFQ.

2.2. Analytical

2.2.1. UV/Visible spectra

The UV/Visible spectrophotometry was applied to collect the UV/Visible spectra of the D1 and D2 soluble complexes with TCNQ and TFQ acceptors in the investigated solvents. These electronic spectra were helpful for:

(i) Characterization of the CT phenomena between the donors (D1 and D2) and the acceptors (TCNQ and TFQ) in different solvents.
(ii) Identification of the charge transfer (CT) electronic absorption band that characterize the D1-TCNQ, D2-TCNQ, D1-TFQ, and D2-TFQ soluble complex in each solvent.
**Fig. 3.** Color of the TCNQ solution in the MeOH (1), MeCN (2), CH$_2$Cl$_2$ (4), and CHCl$_3$ (5) solvents.

**Fig. 4.** Color of the TFQ solution in the MeOH (1), EtOH (2), MeCN (3), CH$_2$Cl$_2$ (4), and CHCl$_3$ (5) solvents.

**Fig. 5.** The UV/Vis spectra of the TCNQ acceptor in the MeOH, MeCN, CH$_2$Cl$_2$, and CHCl$_3$ solvents.

**Fig. 6.** The UV/Vis spectra of the TFQ acceptor in the MeOH, EtOH, MeCN, CH$_2$Cl$_2$, and CHCl$_3$ solvents.
(iii) Verify the wavelength (in nm) corresponding to the CT electronic absorption band ($\lambda_{CT}$) for all soluble CT complexes.

To obtain the UV/Visible spectra, first, standard solutions of D1, D2, TCNQ, and TFQ were prepared in a specific solvent (MeOH, EtOH, MeCN, CH$_2$Cl$_2$, and CHCl$_3$) ($5 \times 10^{-4}$ M). Second, the D1-TCNQ, D2-TCNQ, D1-TFQ, and D2-TFQ systems in each solvent were prepared by mixing equal amounts (1 mL) of the donor and acceptor standard solutions in a 5 mL volumetric flask and completing the volume up to the mark by the solvent. Finally, all the prepared systems were scanned using a Cary 7000 UV–vis–NIR Spectrophotometer from Agilent Technologies, Australia, in the 200–800 nm region. The electronic features of each CT system were obtained by comparing the UV/Visible spectra of the systems with those of the corresponding free components (D1, D2, TCNQ, and TFQ).

2.2.2. Infrared (IR) spectra

The IR spectrophotometry was applied to obtain the IR spectra of the D1 and D2 solid CT complexes with the acceptors in the investigated solvents. Observing and analyzing the IR spectra of the formed CT complexes were helpful for:

i) Observing the changes in the characteristic IR spectral bands of free reactants after the complexation process.

| Compound       | Wavelength of the characteristic absorption bands (nm) |
|----------------|-------------------------------------------------------|
|                | UV MeOH, EtOH MeCN CH$_2$Cl$_2$, CHCl$_3$ | Vis MeOH, EtOH MeCN CH$_2$Cl$_2$, CHCl$_3$ |
| TCNQ acceptor  | 339 – – 394 394 400                                  |
| TFQ acceptor   | 287 333 337 362, 340 487 –                             |
| D1–TCNQ complex| 343 394 394 400                                      |
| D2–TCNQ complex| 342 – – 394 394 400                                   |
| D1–TFQ complex | 289 333 337 362, 340 487 –                             |
| D2–TFQ complex | 289 333 337 362, 340 487 –                             |

Fig. 7. The UV/Vis spectra of the D1–TCNQ complex in MeOH, MeCN, CH$_2$Cl$_2$, and CHCl$_3$ solvents alongside with their free reactants.
ii) Confirming the CT interaction between D1 and D2 with TCNQ and TFQ acceptors in each solvent.

iii) Proposing the suitable mechanisms of the investigated CT interactions.

To obtain the IR spectra, concentrated solutions of D1, D2, TCNQ, and TFQ (2 mmol in 20 mL solvent) were prepared in a specific solvent (MeOH, EtOH, MeCN, CH₂Cl₂, and CHCl₃). Second, the concentrated D1 and D2 solutions were mixed with the corresponding acceptor concentrated solution to generate the D1-TCNQ, D2-TCNQ, D1-TFQ, and D2-TFQ systems. These systems were well-stirred for ~3 min at room temperature and left overnight. Third, the generated colored precipitates were removed from the beakers using filter paper, washed three times with the solvent, and oven-dried. Finally, the solid CT complexes were scanned from 400 to 4000 cm⁻¹ using an ALPHA Bruker Fourier-Transform Infrared Spectrometer from Bruker Optik GmbH, Germany. The vibrational features of each complex were obtained by comparing the IR spectra of the solid products with those of the corresponding free components (D1, D2, TCNQ, and TFQ).

2.2.3. Elemental analysis

A PerkinElmer Microanalyzer (model 2400 Series II CHNS; USA) determined the carbon, hydrogen, and nitrogen contents (%) for the D1-TCNQ, D2-TCNQ, D1-TFQ, and D2-TFQ solid CT complexes. The elemental composition results were used to verify the molar ratio of the CT reaction between D1 and D2 with the investigated acceptors (TCNQ and TFQ).

2.3. Stoichiometric of the CT reaction in solution state

The stoichiometric of the CT reaction between D1 and D2 with the investigated accepting-molecules (TCNQ and TFQ) in the solution state was obtained using two well-known methods: the spectrophotometric titration method and Job’s continuous variation method.

3. Results and discussion

3.1. UV/Visible absorption properties

3.1.1. Free reactants

We found that D1 and D2 donor molecules need slight heat to be dissolved in MeCN, CH₂Cl₂, and CHCl₃ solvents, but in MeOH and EtOH solvents, they completely dissolved without any heat. D1 and D2’s solutions in all solvents were colorless. In contrast, the TFQ acceptor is completely soluble in all solvents without any heat, whereas the TCNQ acceptor is easily dissolved in MeCN.
solvent and needs gentle heat to be soluble in the MeOH, CH$_2$Cl$_2$ and CHCl$_3$ solvents, but it is not soluble in EtOH solvent. Figs. 3 and 4 present the colors of the TCNQ and TFQ solution in the investigated solvents (1.0 × 10$^{-3}$ M), respectively. Both figures indicate that all the TCNQ and TFQ solutions were colored, and the color varied according to the solvent. The electronic spectra of TCNQ and TFQ acceptors in each solvent (MeOH, EtOH, MeCN, CH$_2$Cl$_2$, and CHCl$_3$) are shown in Figs. 5 and 6, respectively.

The TCNQ electronic absorption properties can be classified into two groups:
(a) TCNQ in the MeOH solvent:

The TCNQ acceptor creates a light green solution in MeOH solvent. TCNQ in MeOH solvent behaves differently from the other solvents (MeCN, CH2Cl2, and CHCl3). The shape and intensity of the UV/Visible spectrum of the TCNQ in MeOH are different from those in the other solvents. Methanolic solution of TCNQ exhibits two intense broad bands that look like a plateau. These two bands centered at 339 and 394 nm. The band’s intensity at 339 nm is higher than that at 394 nm. There is also a small broad absorption band found around 740 nm exists in the spectrum of the TCNQ in MeOH.

Fig. 10. The UV/Vis spectra of the D2–TFQ complex in MeOH, EtOH, MeCN, CH2Cl2, and CHCl3 solvents alongside with their free reactants.
(b) TCNQ in the MeCN, CH$_2$Cl$_2$ and CHCl$_3$ solvents:

TCNQ solution in the MeCN, CH$_2$Cl$_2$, and CHCl$_3$ solvents displayed a single, strong, and intense absorption band. This band has a small shoulder band in all solvents. The width of the band is approximately the same in all solvents, around $\sim$60 nm in width. The maximum of the band ($\lambda_{\text{max}}$) is 394 nm in MeCN solvent and 400 nm in CH$_2$Cl$_2$ and CHCl$_3$ solvents.

Also, the TFQ electronic absorption properties can be classified into three groups:

(a) TFQ in the MeOH and EtOH solvents:

TFQ acceptor creates a beige solution in MeOH and EtOH solvents. TFQ behaved similarly in these two solvents. It created two absorption bands. A sharp and very strong band appeared at 287 nm in both solvents, and this sharp band was coupled with a less intense broadband ranging from 330 to 485 nm. The shape of the broadband is slightly different; in MeOH solvent, it looks like a dome ($\lambda_{\text{max}} = 362$ nm), but in EtOH solvent, it looks like a plateau ($\lambda_{\text{max}} = 340$ nm).

(b) TFQ in the MeCN solvent:

The TFQ acceptor forms a remarkable solution in MeCN solvent compared with its solution in other solvents. The color of TFQ's solution in MeOH, EtOH, CH$_2$Cl$_2$, and CHCl$_3$ solvents ranged from beige to light-yellow, but in MeCN solvent, TFQ gives a distinguish light-pink color. TFQ's solution in MeOH, EtOH, CH$_2$Cl$_2$, and CHCl$_3$ solvents absorbs until 485 nm, but in its acetonitrile solution, its absorption extended to 600 nm. Two absorption bands appeared in the spectrum of TFQ's solution in MeCN solvent. These bands were accumulated at 332 and 487 nm. Both bands were broad, but the band's intensity at 332 nm is 5-times that at 487 nm. The band at 332 nm was coupled with a small shoulder band at 287 nm. This shoulder appears as a very strong and sharp band in the spectrum of TFQ's solution in MeCN solvent.

(c) TFQ in the CH$_2$Cl$_2$ and CHCl$_3$ solvents:

A single board absorption band was found in the UV/Visible spectra of TFQ's solutions in CH$_2$Cl$_2$ and CHCl$_3$ solvents. This broad-
Table 2

Values of $E_g$ derived from Tauc’s plots for acceptors alone and their CT complexes with D1 and D2.

| Compound       | $E_g$ (eV) |
|----------------|------------|
|                | MeOH | EtOH | MeCN | CH₂Cl₂ | CHCl₃ |
| TCNQ acceptor  | 1.99 | –    | 2.79 | 2.83   | 2.80 |
| TFQ acceptor   | 2.28 | 2.32 | 1.72 | 2.69   | 2.58 |
| D1–TCNQ complex| 1.86 | –    | 2.86 | 2.85   | 2.81 |
| D2–TCNQ complex| 2.08 | 2.00 | 1.40 | 2.55   | 2.31 |
| D1–TFQ complex | 2.18 | 2.19 | 1.65 | 2.63   | 2.32 |
| D2–TFQ complex | 2.26 | –    | 2.32 | 2.55   | 2.31 |

Fig. 12. Tauc’s Plots for the TFQ acceptor dissolved in the investigated solvents.
Fig. 13. Comparison of $E_g$ values for TCNQ solutions in the investigated solvents.

Fig. 14. Comparison of $E_g$ values for TFQ solutions in the investigated solvents.

Fig. 15. Tauc's Plots for the D1-TCNQ and D2-TCNQ complexes prepared in the investigated solvents.
Fig. 16. Tauc’s Plots for the D1-TFQ and D2-TFQ complexes prepared in the investigated solvents.
Tauc’s plots for the TCNQ and TFQ acceptors dissolved in the investigated solvents, MeOH > EtOH > MeCN > CHCl3 > CH2Cl2. Wavelengths (in nm) of bands of TFQ’s solutions in different solvents decreased as follows: band at 287 nm. The intensities of the characteristic’s absorption band is in the range of 280–420 nm, and it has a weak shoulder. TFQ were dissolved in MeOH, EtOH, MeCN, CHCl3, and CH2Cl2 solvents alongside that of the free reactants, respectively. The derived values of Eg are tabulated in Table 2. The Eg value of the TCNQ and TFQ acceptors depends on the solvent’s type, as indicated in Figs. 13 and 14. The highest Eg value was displayed by TCNQ solution dissolved in CH2Cl2 solvent, where the methanolic solution of TCNQ had the lowest value of Eg. Interestingly, the TFQ acceptor shows the same outcome. Its solution in CH2Cl2 solvent had the highest Eg value, whereas its solution in MeOH solvent had the lowest Eg value. Tauc’s Plots for the D1–TCNQ and D2–TCNQ complexes are shown in Fig. 16. The derived Eg values for D1-TCNQ, D2-TCNQ, D1-TFQ, and D2-TFQ complexes are tabulated in Table 2. The complexation of TCNQ acceptor with D1 slightly increased the value of Eg in all solvents, but when TCNQ was complexed with D2, the value of Eg was slightly decreased in all solvents. In contrast, the complexation of TFQ acceptor with both D1 and D2 slightly decreased the value of Eg in all solvents.

### 3.3. Stoichiometric of the CT interactions

The stoichiometric CT reactions between D1 and D2 with the investigated accepting-molecules (TCNQ and TFQ) in the solid-state were verified by the elemental analyses and spectrophotometric titration and Job’s continuous analysis variation methods in the solution state. The elemental results (C%, N%, and H%) for the D1–TCNQ, D2–TCNQ, D1–TFQ, and D2–TFQ complexes are collected by a PerkinElmer Microanalyzer are listed in Table 3. The collected elemental results proposed that the CT interactions between D1 with TCNQ and TFQ and D1 with TCNQ and TFQ proceed at a 1:1 M ratio in all investigated solvents. The spectrophotometric titration method and Job’s continuous variation method are the most common techniques used to verify the stoichiometry of a chemical reaction in solution state using UV/Vis absorption spectra. Figs. 17 and 18 represent the composition of D1 and D2 with TCNQ and TFQ acceptors in the investigated solvents obtained by the spectrophotometric titration method, respectively. Figs. 19 and 20 represent the composition of D1 and D2 with TCNQ and TFQ acceptors in the investigated solvents obtained by Job’s continuous variation method, respectively. All plots in Figs. 17–20 suggest that the CT interactions between D1 with TCNQ and TFQ and between D1 with TCNQ and TFQ in solution-state proceeds with a

### 3.1.2. CT complexes

Figs. 7 and 8 contain the UV/Vis spectra of the D1–TCNQ and D2–TCNQ complexes in the MeOH, MeCN, CH2Cl2, and CHCl3 solvents alongside that of the free reactants, respectively. The corresponding spectra of the D1–TFQ and D2–TFQ complexes are presented in Figs. 9 and 10, respectively. Generally, D1 and D2 molecules have similar chemical structures. The main difference between the two molecules is that the D2 molecule possesses a C–F bond, whereas the D1 molecule does not. This structure similarity reflects the similarity of the chemical behavior of D1 and D2 molecules when complexed with TCNQ and TFQ acceptors in all solvents. In general, the generation of a CT complex is characterized by a pronounced change in the solution color during the mixing of the donor and the acceptor solutions in an appropriate solvent. This change in solution color is coupled with the change in the electronic spectra of the free donor or/and free acceptor. The spectral changes could be either a new absorption band that did not exist in the electronic spectrum of free donor and free acceptor, an increase in the intensity of the characteristic band referred to the donor or the acceptor, or both. Analysis of the UV/Vis spectra of the D1–TCNQ, D2–TCNQ, D1–TFQ, and D2–TFQ complexes presented in Figs. 7–10 revealed that the CT complexation of D1 and D2 with TCNQ acceptor in MeOH, MeCN, CH2Cl2, and CHCl3, and the CT complexation of D1 and D2 with TFQ acceptor in MeOH, EtOH, MeCN, CH2Cl2, and CHCl3 strongly enhanced the intensity of the characteristic bands of free TCNQ and TFQ acceptors in the specific solvent.

### 3.2. Bandgap energies

Tauc’s plot [123–125] was used to determine the minimum energy for an electron to jump from a valence band to a conduction band; bandgap energy (termed as Eg). Figs. 11 and 12 contain the Tauc’s plots for the TCNQ and TFQ acceptors dissolved in the investigated solvents, respectively. The derived values of Eg are tabulated in Table 2. The Eg value of the TCNQ and TFQ acceptors depends on the solvent’s type, as indicated in Figs. 13 and 14. The highest Eg value was displayed by TCNQ solution dissolved in CH2Cl2 solvent, where the methanolic solution of TCNQ had the lowest value of Eg. Interestingly, the TFQ acceptor shows the same outcome. Its solution in CH2Cl2 solvent had the highest Eg value, whereas its solution in MeOH solvent had the lowest Eg value. Tauc’s Plots for the D1–TCNQ and D2–TCNQ complexes are shown in Fig. 16. The derived Eg values for D1-TCNQ, D2-TCNQ, D1-TFQ, and D2-TFQ complexes are tabulated in Table 2. The complexation of TCNQ acceptor with D1 slightly increased the value of Eg in all solvents, but when TCNQ was complexed with D2, the value of Eg was slightly decreased in all solvents. In contrast, the complexation of TFQ acceptor with both D1 and D2 slightly decreased the value of Eg in all solvents.
molar ratio of 1:1 in all solvents, as observed in the solid-state interaction between the pair components (D1 and TCNQ; D2 and TFQ; D1 and TFQ). 

3.4. Determining spectroscopic parameters

Four common spectroscopic parameters were determined. These parameters were the molar absorptivity ($\varepsilon_{\text{max}}$), formation constant ($K_{\text{CT}}$), transition dipole moment ($\mu_{\text{eg}}$), and oscillator strength ($f$) [126–128]. The units of $\varepsilon_{\text{max}}$, $K_{\text{CT}}$, and $\mu_{\text{eg}}$ parameters are (L mol$^{-1}$ cm$^{-1}$), (L mol$^{-1}$), and (Debye), respectively. The $\varepsilon_{\text{max}}$, $K_{\text{CT}}$, $\mu_{\text{eg}}$, and $f$ parameters were calculated for the D1–TCNQ, D2–TCNQ, D1–TFQ, and D2–TFQ complexes in the investigated solvents to understand the CT characteristics from D1 and D2 molecules towards TCNQ and TFQ molecules. Graphical representation of the 1:1 Benesi-Hildebrand equation for the D1 and D2 interactions with TCNQ and TFQ in various solvents are presented in Figs. 21 and 22, respectively. Table 4 lists the derived values of the spectroscopic parameters ($K_{\text{CT}}$, $\varepsilon_{\text{max}}$, $\mu_{\text{eg}}$, and $f$) for the D1–TCNQ, D2–TCNQ, D1–TFQ, and D2–TFQ complexes. All the synthesized complexes had high values of $K_{\text{CT}}$. The $K_{\text{CT}}$ values for the complexes lie in the range from $1.8 \times 10^6$ to $8.8 \times 10^6$ L mol$^{-1}$. D1 and D2 complexes with TCNQ acceptor had very high values of $\mu_{\text{eg}}$ and $f$ parameters compared with their complexes with TFQ acceptor.

Fig. 17. The composition of D1 and D2 with TCNQ acceptor in the investigated solvents (MeOH, MeCN, CH$_2$Cl$_2$, and CHCl$_3$) determined by the spectrophotometric titration method.
for CT transitions \[38,69,76,88,102,111,122\]. A strong, positive linear correlation between D1 and D2 molecules displayed several absorption bands. D1 and D2 molecules possess multiple CH2 and CH3 groups [eight CH2 groups and two CH3 groups in D1; five CH2 groups and three CH3 groups in D2], and these groups make the IR spectrum of D1 and D2 noise complicated, especially in the area from 700 to 1500 cm\(^{-1}\). The bending vibrations of CH2 groups: \(\delta_{\text{twi}}(\text{CH}_2), \delta_{\text{wag}}(\text{CH}_2), \delta_{\text{rock}}(\text{CH}_2)\), and \(\delta_{\text{bend}}(\text{CH}_2)\) are responsible for the bands located at 566, 779, 1277, and 1351 cm\(^{-1}\) in the IR spectrum of D1, respectively. The corresponding wavenumbers for the D2 were 612, 897, 1403, and 1448 cm\(^{-1}\), respectively [129,130,131]. The bending vibrations of CH3 groups: \(\delta_{\text{rock}}(\text{CH}_3), \delta_{\text{wag}}(\text{CH}_3), \delta_{\text{twi}}(\text{CH}_3), \delta_{\text{bend}}(\text{CH}_3)\) are responsible for the bands located at 566, 779, 1277, and 1351 cm\(^{-1}\) in the IR spectrum of D1, respectively. The corresponding wavenumbers for the D2 were 612, 897, 1403, and 1448 cm\(^{-1}\), respectively. The \(\nu(C=O)\) vibrations create a broad absorption band with a medium-intensity accumulation at 2946 cm\(^{-1}\) (D2) and 2920 cm\(^{-1}\) (D1). The in-plane bending, out-of-plane bending, and stretching vibrations generated from the O–H bonds in the D1 molecule created the bands at 685, 936, and 3414 cm\(^{-1}\), respectively. The corresponding wavenumbers for the D2 were 690, 984, and 3393 cm\(^{-1}\), respectively.

In the IR spectrum of pure TCNQ, the band at 2216 cm\(^{-1}\), combined with a small broad shoulder at 2282 cm\(^{-1}\), resulted from the molecule’s \(\nu(C=\text{N})\) vibrations. The four C–H bonds in the TCNQ are absorbed in 855, 1350, 2968, and 3046 cm\(^{-1}\) due to the \(\delta_{\text{rock}}(-\text{C–H}), \delta_{\text{def}}(\text{C–H}), \nu_{\text{as}}(\text{C–H}), \nu_{\text{as}}(\text{C–H})\) modes, respectively. The bands registered at (1052 and 1118) and 1533 cm\(^{-1}\) were generated from the \(\delta(\text{C–C})\) and \(\nu(\text{C–C})\) vibrations, respectively. The functional groups in the TFQ molecule are two C=C, two C=O, and four C–F. In the IR spectrum of this molecule, the three types of chemical bonds created three intense and very strong bands, registered respectively at 1320, 1680, and 988 cm\(^{-1}\), caused by the \(\nu(\text{C=C}), \nu(\text{C=O}), \nu(\text{C–F})\).
Fig. 19. The composition of D1 and D2 with TCNQ acceptor in the investigated solvents (MeOH, MeCN, CH$_2$Cl$_2$, and CHCl$_3$) obtained by the Job’s continuous variation method.
Fig. 20. The composition of D1 and D2 with TFQ acceptor in the investigated solvents (MeOH, MeCN, CH₂Cl₂, and CHCl₃) determined by the Job's continuous variation method.
**Fig. 21.** Graphical representation of the 1:1 Benesi-Hildebrand equation for the D1 and D2 interactions with TCNQ acceptor in the investigated solvents (MeOH, MeCN, CH$_2$Cl$_2$, and CHCl$_3$).
Fig. 22. Graphical representation of the 1:1 Benesi–Hildebrand equation for the D1 and D2 interactions with TFQ acceptor in the investigated solvents (MeOH, EtOH, MeCN, CH₂Cl₂, and CHCl₃).
TCNQ and TFQ molecules are typical electron-accepting units because they contain strong terminal electron-withdrawing groups. When a molecule possesses terminal electron-withdrawing groups, they take the electron density from the molecule’s core, making the core deficient in electron density and thirsty to accept electronic charges from another molecule (electron-donating molecule). The terminal electron-withdrawing groups in TCNQ are the four C=N groups and are the two C=O and four C=F groups in TFQ. These withdrawing groups greatly decrease the electron density of the TCNQ and TFQ’s aromatic rings and increase the aromatic ring’s need for electrons. When mixing solutions of D1 or D2 with solutions of TCNQ or TFQ, electron charges were transferred from the donating sites in the electron-donating molecule (D1 or D2) to the aromatic ring of the electron-accepting molecule (TCNQ or TFQ) [D1 → TCNQ; D2 → TCNQ; D1 → TFQ; D2 → TFQ]. This donating-accepting interaction affects the solution’s color, the distinguish electronic spec-

| Solvent   | D1–TCNQ complex | D2–TCNQ complex | D1–TFQ complex | D2–TFQ complex |
|-----------|-----------------|-----------------|----------------|----------------|
|           | \( \lambda_{\text{max}} \) (nm) | \( \epsilon_{\text{max}} \) (L mol\(^{-1}\) cm\(^{-1}\)) | \( K_{\text{CT}} \) (L mol\(^{-1}\)) | \( \mu \) (Debye) | \( f \) | \( \lambda_{\text{max}} \) (nm) | \( \epsilon_{\text{max}} \) (L mol\(^{-1}\) cm\(^{-1}\)) | \( K_{\text{CT}} \) (L mol\(^{-1}\)) | \( \mu \) (Debye) | \( f \) |
| MeOH      | 394             | 7.85 \times 10^5 | 4.44 \times 10^6 | 21.7 | 0.565 | 394 | 8.10 \times 10^5 | 1.94 \times 10^6 | 22.1 | 0.582 |
| MeCN      | 394             | 2.54 \times 10^6 | 2.57 \times 10^6 | 39.2 | 1.831 | 394 | 3.11 \times 10^5 | 3.96 \times 10^6 | 43.3 | 2.235 |
| CH\(_2\)Cl\(_2\) | 400            | 3.12 \times 10^6 | 1.94 \times 10^6 | 43.6 | 2.242 | 400 | 3.01 \times 10^5 | 2.62 \times 10^6 | 42.9 | 2.168 |
| CHCl\(_3\) | 400             | 3.68 \times 10^6 | 7.55 \times 10^6 | 47.4 | 2.646 | 400 | 2.78 \times 10^6 | 2.15 \times 10^6 | 41.2 | 1.999 |
| D1–TFQ complex | \( \lambda_{\text{max}} \) (nm) | \( \epsilon_{\text{max}} \) (L mol\(^{-1}\) cm\(^{-1}\)) | \( K_{\text{CT}} \) (L mol\(^{-1}\)) | \( \mu \) (Debye) | \( f \) | \( \lambda_{\text{max}} \) (nm) | \( \epsilon_{\text{max}} \) (L mol\(^{-1}\) cm\(^{-1}\)) | \( K_{\text{CT}} \) (L mol\(^{-1}\)) | \( \mu \) (Debye) | \( f \) |
| MeOH      | 362             | 4.36 \times 10^5 | 4.69 \times 10^6 | 12.00 | 0.188 | 362 | 2.64 \times 10^5 | 1.85 \times 10^6 | 9.37 | 0.114 |
| EtOH      | 340             | 3.93 \times 10^5 | 7.71 \times 10^6 | 11.08 | 0.170 | 340 | 3.02 \times 10^5 | 1.86 \times 10^6 | 9.70 | 0.130 |
| MeCN      | 333             | 3.24 \times 10^5 | 1.79 \times 10^6 | 11.12 | 0.175 | 333 | 4.18 \times 10^5 | 6.97 \times 10^6 | 12.63 | 0.226 |
| CH\(_2\)Cl\(_2\) | 337        | 3.82 \times 10^5 | 8.88 \times 10^6 | 12.16 | 0.207 | 337 | 3.92 \times 10^5 | 5.48 \times 10^6 | 12.30 | 0.212 |
| CHCl\(_3\) | 337             | 2.89 \times 10^5 | 1.86 \times 10^6 | 10.58 | 0.156 | 337 | 2.91 \times 10^5 | 1.97 \times 10^6 | 10.60 | 0.157 |

Fig. 23. Linear relationship between oscillator strength (\( f \)) and transition dipole moment (\( \mu \)).

Fig. 24a. IR spectra of free D1 and D2 molecules.
tral bands of the free reactants, and the distinguish IR spectral bands of the free reactants.

The IR spectra displayed in Fig. 25 are for the solid D1–TCNQ, D2–TCNQ, D1–TFQ, and D2–TFQ complexes generated in different solvents. These IR spectra revealed several spectral changes in the distinguish IR bands of free reactants (D1, D2, TCNQ, TFQ) after the CT complexation. Here we mentioned three examples: i) The bands resulting from the C=O stretching vibrations of the carbonyl and carboxylic groups of free D1 and D2 shifted to lower frequencies after CT complexation with TCNQ and TFQ. From 1704–1642 cm\(^{-1}\) in the free D1 to around \(\sim 1686–1630\) cm\(^{-1}\) in the D1–TCNQ and D1–TFQ complexes. The same was detected for the D2: the bands were moved from 1713–1660 cm\(^{-1}\) to around \(\sim 1700–1642\) cm\(^{-1}\) in the D2–TCNQ and D2–TFQ complexes. ii). The CT complexation between TCNQ with D1 and D2 affected the intensity and position of the characteristic bands belonging to the \(\nu(C\equiv N)\) in the free TCNQ. The position of the bands was moved from 2216 and 2282 cm\(^{-1}\) in the free TCNQ to around \(\sim 2190\) and 2210 cm\(^{-1}\) in its complexes with D1 and D2 (D1–TCNQ, D2–TCNQ). iii) In the free TFQ, the \(\nu(C\equiv F)\) vibrations resonated at 988 cm\(^{-1}\) as a very strong, intense band, but in the D1–TFQ and D2–TFQ complexes, this was appeared at around \(\sim 1020\) cm\(^{-1}\) as a medium intensity band.

4. Conclusions

Hydrocortisone (D1) and dexamethasone (D2) have received considerable attention because they are widely used to treat COVID-19. We aim to furnish a big-picture perspective on the charge-transfer (CT) properties of corticosteroids D1 and D2. In part I, we examined the CT property of D1 and D2 towards the DDQ accepting-molecule in five different organic solvents. This part (part II) described the CT reaction between D1 and D2 with two new organic accepting-molecules (TCNQ and TFQ) in five different organic solvents. Calculated values of oscillator strength (\(f\)) and transition dipole moment (\(\mu_{\text{eg}}\)) suggested that the interaction between the investigated corticosteroids with TCNQ acceptor is much stronger than their interaction with TFQ acceptor. IR measurements suggested that electron charges transferred from the donating sites in D1 and D2 to the aromatic ring of TCNQ and TFQ (\(n \rightarrow \pi^*\) transitions).
CRediT authorship contribution statement

Moamen S. Refat: Data curation, Funding acquisition, Project administration, Writing – original draft, Writing – review & editing. Bander Albogami: Supervision, Conceptualization, Software, Validation, Visualization. Abdel Majid A. Adam: Data curation, Funding acquisition, Project administration, Writing – original draft, Writing – review & editing. Hosam A. Saad: Investigation, Formal analysis, Methodology, Resources. Amnah Mohammed Alsuhaibani: Investigation, Formal analysis, Methodology, Resources. Lal Miyan: Supervision, Conceptualization, Software, Validation, Visualization. Mohamed S. Hegab: Investigation, Formal analysis, Methodology, Resources.

Data availability

Data will be made available on request.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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