CHARGE TRANSFER MOLECULAR COMPLEXES OF 4-(DIMETHYLAMINO)PYRIDINE WITH SOME CONVENTIONAL AND UNCONVENTIONAL ACCEPTORS INVOLVING FLUOROARENES

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Charge transfer (CT) complexes of 4-(dimethylamino)pyridine (DMAP) with iodine as a typical σ-type acceptor and with typical π-type acceptor, 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ), have been synthesized and characterized. Octafluorotoluene (OFT), octafluoronaphthalene (OFN), perfluorophenanthrene (PFP), and 2,3,5,6-tetrafluoropyridine-4-carbonitrile (TFP) were also used as acceptors for interaction with DMAP. Properties of such CT complexes were investigated by UV/VIS and IR spectra, and elemental analyses of the isolated complexes. The systems DMAP–iodine and DMAP–DDQ are characterized by formation of triiodide ions (I_3^-) and $DDQ^{\bullet -}$ anion radicals, respectively, which is proposed to occur via initial formation of outer-sphere CT complexes. The systems (DMAP–OFT, DMAP–OFN, DMAP–PFP and DMAP–TFP) are characterized by the appearance of new UV/VIS spectral bands assigned as CT bands; they also furnished the corresponding solid complexes with the stoichiometric ratio 1:1. ^1H and ^{19}F NMR spectra were used on confirming the formation of the DMAP–PFP CT complexes. The formation constants (K_{CT}) and molar absorption coefficients (ε_{CT}) of the latter complex were obtained.

Keywords: Charge transfer complexes; CT complexes; 4-(Dimethylamino)pyridine (DMAP); Fluoroarenes acceptors; Formation constants; UV-VIS spectroscopy.

The ozone depletion potential of chlorofluorocarbons[1,2] (CFCs) and the importance of fluoroorganic compounds for industrial applications[3–5] encouraged me to perform this piece of work. Fluoroarenes, hexafluorobenzene[6–9] and fluoranil[9–13], and some fluoroalkanes[14] are known as charge transfer (CT) acceptors. Thus, LUMO of fluorocarbon compounds can accept charges or even electrons from the HOMO of donors. Perfluoroarenes involving perfluoronaphthalene and perfluorophenanthrene have produced significant crystals of CT complexes[15,16] with some selected ferrocenes, but no CT spectral bands could be identified in these systems. This piece of work was performed to study the CT interaction of fluoroarenes with one of the known and strong donors, 4-(dimethylamino)pyridine[17,18] (DMAP). DMAP

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and its planar-chiral derivatives represent significant milestones in the research of low-molecular-weight compounds that can serve as alternatives to enzymes in many nucleophilic-catalyzed transformations[19–22]. A notable interest of our research team is the time dependence of the CT UV/VIS spectral band(s) in some cases of CT interactions. We have shown[23,24] that a new acceptor formed in situ during the donor–acceptor interaction is responsible for this time dependence. For this purpose, both iodine (I_2) and 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ), well-known σ- and π-acceptors, are selected in this study to screen the interactions with the donor (DMAP), especially from the time-dependence point of view. Each of these acceptors has distinct and definite characteristics in their different forms[25–32].

EXPERIMENTAL

Materials and Solutions

The electron donor, 4-(dimethylamino)pyridine (DMAP), was purchased from Aldrich Chemical Co. and it was used without further purification. The electron acceptor, 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) (Aldrich Chemical Co.), was recrystallized from both chlorobenzene and dry methylene chloride, respectively, whereas iodine (Merck AG) was resublimed under reduced pressure. The fluorocarbon compounds, octafluorotoluene (OFT), octafluoronaphthalene (OFN), perfluorophenanthrene (PFP), and 2,3,5,6-tetrafluoropyridine-4-carbonitrile (TFP) were purchased from Aldrich Chemical Co. and used without further purification. The solvents were of pure spectral grade (BDH or Merck).

Physical Measurements

The electronic absorption spectra were recorded on a Perkin–Elmer Lambda 40 spectrophotometer equipped with a Julabo FP 40 thermostat (±0.1 °C) using 1.0 cm matched quartz cells. IR spectra of the solid CT complexes were recorded on a Shimadzu IR-408 spectrophotometer. ^1H NMR spectra were recorded on a GE-Omega 300 MHz spectrometer and referenced to an internal residual solvent peak (^1H). ^{19}F NMR spectra were determined on a Bruker Y-490 MHz with CCl_3F as an external standard. Computations were performed making use of both the Benesi–Hildebrand[33] and Scott[34] methods with the aid of two programs based on unweighted linear least-squares fits. Stock solutions of the donor or acceptors in proper solvents were freshly prepared prior to use. For determination of the formation constants (K_{CT}) and molar absorption coefficients (ε_{CT}) of the CT complexes by applying the Benesi–Hildebrand[33] and Scott[34] methods, spectra of the CT mixtures were collected after mixing solutions of the donor and acceptor and elapsing the time necessary to reach maximum absorption intensity, whereas the concentration of the acceptor was kept constant, $[A] = 1.0 \times 10^{-3}$ mol dm^{-3}, meanwhile, the concentration of the donor varied, $[D] = 4.0 \times 10^{-2}$ to 2.0×10^{-3} mol dm^{-3}, at least nine mixtures solutions. Elemental analyses for C, H, N and Cl of the solid complexes were carried out in the microanalytical laboratory, Cairo University, Cairo, Egypt. The I contents were estimated by the conventional spectrophotometric method.

Synthesis of the Solid CT Complexes

The solid CT complex of iodine with the donor (DMAP) was synthesized by mixing a methylene chloride solution of I_2 (1.015 g) with that of DMAP (0.513 g), and the resulting complex solution was left standing at room temperature overnight. The solid complex was separated as fine crystals (1.203 g, 80%) with the stoichiometric ratio 1:1 donor:acceptor. On the other hand, the solid 1:1 CT complex of the DMAP with DDQ was prepared by mixing the required amount of the donor (0.611 g) dissolved in a minimum amount of CH_2Cl_2 with an appropriate amount of the acceptor (1.135 g) in the 1:1 mole ratio. The mixture was refluxed for 2 h. The solid separated by cooling the solution was washed several times with CH_2Cl_2. The precipitate was collected and recrystallized from absolute ethanol and dried (1.342 g, 65%).

Complexes of the DMAP donor with the fluorocarbon acceptors (OFN, PFP, and TFP) were prepared by mixing CH_2Cl_2 solutions of the donor (0.611 g) and each acceptor in the ratio 1:1 (1.36 g, 1.791 g, and 0.88 g of OFN, PFP, and TFP, respectively). The mixtures were refluxed for 2–3 h and cooled. The precipitates were collected and recrystallized from CH_2Cl_2–hexane mixtures and dried. All the prepared complexes have the stoichiometric ratio 1:1:1 donor:acceptor:water; DMAP–OFN 0.62 g (30%); DMAP–PFP 0.82 g (33%); DMAP–TFP 0.443 g (28%). Attempts to prepare solid CT complex (DMAP–OFT) have so far been unsuccessful.

The found elemental analyses of the complexes were in satisfactory agreement with the calculated values:

(DMAP–I_2). For $C_{14}H_{20}I_4N_4$ (752.0) calculated: 22.36% C, 2.66% H, 67.53% I, 7.45% N; found: 22.93% C, 2.82% H, 67.20% I, 7.15% N.

(DMAP–DDQ). For $C_{15}H_{10}Cl_2N_4O_2$ (349.2) calculated: 51.585% C, 2.89% H, 20.33% Cl, 16.04% N; found: 50.98% C, 3.03% H, 20.12% Cl, 16.11% N.

(DMAP–OFN). For $C_{17}H_{10}F_8N_2 \cdot H_2O$ (412.3) calculated: 49.53% C, 2.93% H, 6.80% N; found: 50.49% C, 3.12% H, 6.45% N.

(DMAP–PFP). For $C_{21}H_{10}F_{10}N_2 \cdot H_2O$ (498.3) calculated: 50.62% C, 2.43% H, 5.62% N; found: 50.81% C, 2.64% H, 5.77% N.

(DMAP–TFP). For $C_{13}H_{10}F_4N_4 \cdot H_2O$ (316.3) calculated: 49.37% C, 3.82% H, 17.72% N; found: 49.33% C, 3.79% H, 17.68% N.

RESULTS AND DISCUSSION

Charge Transfer Interactions of DMAP with I_2 and DDQ

Electronic absorption spectra of CH_2Cl_2 solution mixtures of the DMAP donor with I_2 σ-acceptor or with the DDQ π-acceptor were recorded in the wavelength range 200–700 nm. In all cases, new bands, which do not belong to the donor and each acceptor, appeared. In the case of DMAP–I_2, two new bands at 292 and 363 nm appeared and reached almost maximum intensities after 15 min. These bands are characterized to those of the triiodide ion[23,26,31,32,35,36] (I_3^-). Formation of the triiodide complexes as a result of the interactions of *n*-donors (D) with the σ-acceptor (I_2) has been reported[26,35–37] to follow the following reaction pathway: (i) formation of the associative outer-sphere CT complex DI_2, (ii) transformation to the dissociative inner-sphere complex (DI·I), (iii) association with another iodine molecule to form the triiodide complex ($D^+I \cdot I_3^-$). Thus, the 15 min may be required for completion of this transformation. Meanwhile, the lone pair of electrons on each of the ring nitrogen and/or amino nitrogen atom of the DMPA donor emphasized this interaction pathway although the pK_a values of the aminopyridines, in general, have been shown to correspond to protonation of the ring nitrogen[18,38,39].

The electronic spectrum of a solution of solid complex DMAP–I_2 in CH_2Cl_2 indicates the presence of I_3^- ions[23,26,31,32,35,36]. Also, elemental analysis of the formed solid CT complex of DMAP with I_2 indicated the stoichiometric ratio D:A either 1:1, as previously reported by Daisey et al.[18], or 2:2. Formation of a compound having the triiodide ions means that this compound (complex) contains, definitely, at least 1.5 iodine atoms. In turn, the 2+2 assembly in which two molecules of both donor and acceptors come to bonding each other may be truly describe the case meaning that another molecule of the donor DMAP was somehow bonded with the triiodide complex ($DMAP^+I \cdot I_3^-$). Thus, one can expect that the first formed triiodide complex ($DMAP^+I \cdot I_3^-$) still has the ability to accept charges. It serves as a new acceptor resulting in situ and this undergoes CT interaction with another molecule of the donor to form the solid CT complex ($DMAP) \cdot (DMAP^+I \cdot I_3^-$) having the ratio 1:1 (DMAP):($DMAP^+I \cdot I_3^-$).

A careful investigation of the IR spectrum of the synthesized CT solid complex showed the characteristic peaks[40] of both the free donor (DMAP), except some shift to lower frequencies, and the pyridinium ion ($DMAP^+$), particularly the peaks assigned to the stretching vibrations of C=N and C=C located at 1595 cm^{-1} for DMAP, and 1650 and 1565 cm^{-1} for the pyridinium ion[40] ($DMAP^+$). This may give evidence for the proposed structural formula of the formed CT complex ($DMAP) \cdot (DMAP^+I \cdot I_3^-$).

Thus, one can suggest that the previously reported[23,26,32,35,36] reaction pathway for the formation of the triiodide complexes may be extended by the interaction with another molecule of the donor (DMAP) according to the following scheme:

$$\begin{array}{ccccccccc} \text{DMAP} & + & I_2 & \rightarrow & \text{DMAP}\cdot I_2 & \rightarrow & \text{DMAP}^+I\cdot I^- \\ & & & & \text{(outer-sphere CT complex)} & & \text{(inner-sphere complex)} \end{array}$$

$$\begin{array}{ccccc} \mathrm{DMAP^{+}I{\cdot}I^{-}} & + & \mathrm{I_2} & \rightarrow & \mathrm{DMAP^{+}I{\cdot}I_3^{-}} \\ & & & & \text{(first formed complex)} \end{array}$$

$$\begin{array}{ccccc} \mathrm{DMAP} & + & \mathrm{DMAP^{+}I{\cdot}I_3^{-}} & \rightarrow & \mathrm{(DMAP){\cdot}(DMAP^{+}I{\cdot}I_3^{-})} \\ \text{(donor)} & & \text{(new acceptor)} & & \text{(CT complex)} \end{array}$$

Concerning the interaction between the donor (DMAP) with DDQ, π-acceptor, the recorded spectra for CH_2Cl_2 mixture solutions of DMAP and DDQ displayed a series of absorption bands appearing at λ_{max} = 340, 441, 460, 562, and 605 nm (Fig. 1). These bands are time-dependent reaching stability after about 80 min on mixing the reactant species. Undoubtedly, these bands are ascribed to the anion radicals ($DDQ^{\bullet-}$) based on the peak positions and shapes[25,27,29,30,32,35,41,42]. This means that the DMAP–DDQ complex exists in solution predominantly in the dissociated state radical cations and anions, $DMAP^{\bullet+}$ and $DDQ^{\bullet-}$, respectively.

The appearance of the structural bands characterizing the $DDQ^{\bullet-}$ anion radicals seems to follow the previously reported[32,43–45] interaction pathway. Thus, it can be probably ascribed to transformation of the CT complex from an outer-sphere type of the DMAP–DDQ nonbonding structure to an inner-sphere complex $DMAP^{\bullet+}$–$DDQ^{\bullet-}$ of dative structure. Then equilibrium dissociation to the radicals $DMAP^{\bullet+}$ and $DDQ^{\bullet-}$ is established in the ground state.

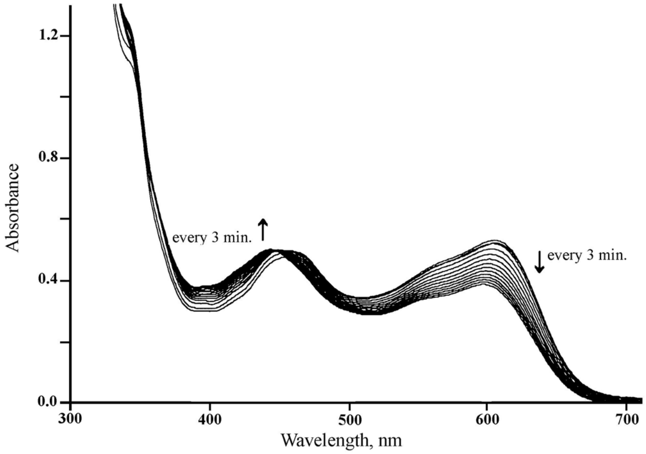

FIG. 1
Electronic absorption spectra of a DMAP–DDQ solution in CH_2Cl_2 at 25 °C. [DMAP] = 4.0×10^{-3} mol dm^{-3}, [DDQ] = 2.0×10^{-4} mol dm^{-3}

As the recorded spectra of this complex are perturbed by those of the anion radicals, they do not exhibit well defined CT band(s), and all attempts to obtain definite CT band(s) did not succeed. Hence, determination of the formation constant of this CT complex is not possible.

Careful examination of IR spectra of the solid complex formed from the donor DMAP and DDQ by comparing with the IR spectra of the free donor DMAP and of the free acceptor DDQ gives evidence[25,30,40,46–48] that the structure of this complex could be represented by $DMAP^{\bullet +}–DDQ^{\bullet -}$. The pyridinium ion ($DMAP^{\bullet +}$) was indicated by the main characteristic[40] IR peaks for C=N and C=C stretching vibrations located at 1650 and 1565 cm^{-1}, respectively. The semiquinone anion ($DDQ^{\bullet -}$) was indicated by its characteristic[25,46–48] peaks located at 2240 cm^{-1} for C≡N stretching vibration and the group bands associated with C–Cl vibration that appeared at 895, 800, and 740 cm^{-1}. In addition, the characteristic peak of the C=O group at 1680 cm^{-1} in the IR spectrum of the free donor (DDQ) disappeared in the IR spectrum of the complex; the acceptor has no longer the quinone form. Besides, the absence of any peaks characteristic of the OH in the wavelength range 3250–3700 cm^{-1} indicates that incomplete reduction of the acceptor to the corresponding hydroquinone (neither $DDQH^-$ nor $DDQH_2$) did not occur.

The electronic absorption spectrum of the dissolved solid complex in methanol showed the same bands previously appearing in the spectra of CH_2Cl_2 solutions of the donor (DMAP) and acceptor (DDQ), except a small shift owing to the solvents polarities. On the other hand, elemental analysis of the formed solid complex indicates the stoichiometric ratio 1:1 of ($DMAP^{\bullet +}–DDQ^{\bullet -}$).

Charge Transfer Complexation Between DMAP and Unconventional Acceptors; Fluorocarbon Compounds

Electronic absorption spectra of CH_2Cl_2 solutions of the donor DMAP with either of octafluorotoluene (OFT), octafluoronaphthalene (OFN), perfluorophenanthrene (PFP), and 2,3,5,6-tetrafluoropyridine-4-carbonitrile (TFP) were recorded in the wavelength range 250–600 nm, and showed new absorption band(s) not belonging to either DMAP or fluorocarbon compound, located at 369, 404, 401, and 390 nm, respectively (Figs 2 and 3). The absorption intensities of the observed bands increased slowly with time reaching maximum constant values after 3 h, ~24 h, 90 min, and 150 min for the bands recorded in solution DMAP–OFT (λ_{max} = 369 nm), DMAP–OFN

(λ_{max} = 404 nm), DMAP–PFP (λ_{max} = 401 nm) (cf. Fig. 2), and DMAP–TFP (λ_{max} = 390 nm) (cf. Fig. 3), respectively. These bands are generally assigned as CT bands arising from the charge transfer from the highest occupied molecular orbital (HOMO) of the DMAP donor to the lowest unoccupied molecular orbital (LUMO) of each of the unconventional acceptors, OFT, OFN, PFP, and TFP, although these bands are time-dependent. The inclusion of a large number of electron-withdrawing atoms inverts the natural electron-donor characteristics of the π-cloud in the aromatic rings[49].

Many pieces of evidence can support the CT interaction for all the studied DMAP/fluorocarbon systems and, also, the time dependence may have an adequate explanation.

(i) A chemical reaction involving breaking of the C–F bond(s) is not the preferable possibility as the C–F σ-bonds are short and too strong

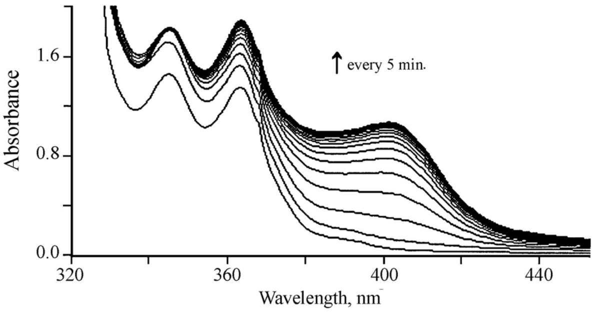

FIG. 2
Electronic absorption spectra of a DMAP–PFP solution in CH_2Cl_2 at 25 °C. [DMAP] = 4.0 × 10^{-2} mol dm^{-3}, [PFP] = 1.0 × 10^{-3} mol dm^{-3}

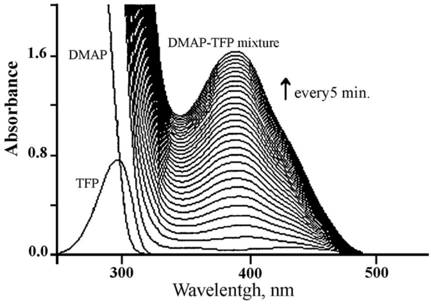

FIG. 3
Electronic absorption spectra of a DMAP–TFP solution in CH_2Cl_2 at 25 °C. [DMAP] = 4.0 × 10^{-3} mol dm^{-3}, [TFP] = 2.0 × 10^{-4} mol dm^{-3}

(for C–F [50], bond length is 1.34 Å, bond strength 552 kJ mol^{-1}, and force constant 7.42 N cm^{-1}) to be broken easily when performing replacement of fluorine atom, particularly under the mild conditions.

(ii) The elemental analyses of the solid complexes synthesized from the donor DMAP and fluorocarbon acceptors (OFN, PFP, and TFP) match the suggested general formula of the 1:1 donor:acceptor.

(iii) The electronic absorption spectra of solutions of solid complexes in CH_2Cl_2 showed the same bands appearing in the recorded spectra of CH_2Cl_2 solutions of each donor/acceptor.

(iv) Careful investigation of the IR spectra brings a set of convincing evidence of the CT interactions. Thus, comparing important IR spectral bands of the free electron donor DMAP and the free electron acceptors (OFN, PFP, and TFP) with those of the corresponding solid products indicated the CT interactions (Fig. 4).

Except the appearance of the bands referring to the pyridinium ions[40] located at around 1650 and 1560 cm^{-1} for the C=N and C=C stretching vibrations and except, also, some reasonable shift in frequencies of functional bands of both the DMAP donor and the acceptors OFN, PFP, and TFP, the IR spectra of the CT complexes seem to superimpose the individual IR spectrum of DMAP and each corresponding acceptor. Thus, the group peaks characteristic of C–F stretching vibrations of the free acceptors located in the frequency range 1000–1300 cm^{-1} are shifted in the IR spectra of the corresponding CT complexes to lower frequencies by 10–50 cm^{-1}.

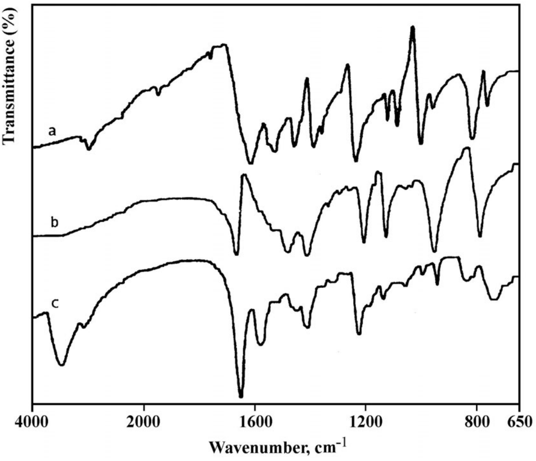

FIG. 4
IR spectra of free DMAP donor (a), free OFN acceptor (b) and DMAP–OFN CT complex (c)

The IR spectrum of the DMAP–TFP showed the very characteristic peak for C≡N stretching vibration at 2250 cm^{-1} indicating that no reduction of the C≡N group of the acceptor (TFP). Meanwhile, any chemical reaction may primarily affect this functional group. The most remarkable observations in the IR spectra of all CT complexes are the appearance of a new peak around 3350 cm^{-1} (cf. Fig. 4), which could be assigned to the OH group.

Thus, one can suggest that each of these CT complexes is consistent with the corresponding acceptor and the quaternary salt of pyridine donor ($DMAPH^+OH^-$). It is worth mentioning that on making a preliminary qualitative diagnostic test for the presence of OH by mixing two methanolic solutions of $FeCl_3$ and the CT complex, a precipitate of $Fe(OH)_3$ appeared indicating the presence of the OH group in the complex. The spectral grade CH_2Cl_2 solvent contains ca. 0.02% of water, so the trace amount of water present in the solvent or even from atmosphere may be attracted to the donor by the charge-withdrawing effect of the acceptors to form the quaternary salt $DMAPH^+OH^-$. Thus, the donor DMAP alone in the solvent does not furnish the corresponding quaternary salt, but the presence of the acceptor(s) may activate or initiate the donor to attract water molecules. Elemental analyses of the formed CT complexes matched the suggested formula $DMAPH^+OH^-$/acceptor with the stoichiometric ratio 1:1 for all CT complexes.

(v) The ^{1}H and ^{19}F NMR spectra presented the persuasive confirmation of the CT interaction. Thus, the ^{1}H and ^{19}F NMR spectra of CT complex on comparing with those (^{1}H NMR) of the free donor and free acceptors (^{19}F NMR) indicate that no chemical reaction between the donor and the acceptor has taken place.

The ^{1}H NMR spectrum of a solution of solid CT complex (DMAP–PFP) in CD_2Cl_2 showed frequencies at δ 6.490, 6.474, 2.988, and 2.964 ppm and these are exactly the same as those of the free donor (DMAP) located at δ 6.490, 6.474, 2.988, and 2.964 ppm, respectively, except an increase in the chemical shift of protons 2 and 6 (at δ 8.154 ppm) in the pyridine ring of the complex DMAP–PFP compared with the donor alone (DMAP, at δ 8.151). This shift is due to the presence of partial positive charge on the ring nitrogen atom, which causes deshielding of the neighboring protons 2 and 6.

Also ^{19}F NMR spectra proved that the formed CT complex (DMAP–PFP) has the same fluorine atoms as the free acceptor PFP, i.e. CT interaction. Thus, the ^{19}F NMR spectrum of a solution of the complex DMAP–PFP in CD_2Cl_2 showed the resonance frequencies at δ –144.81, –144.84, –144.98, –145.02, –145.73, –145.90, –152.14, –152.18, –152.23, –153.62, and

–153.72 ppm, and these are the corresponding peaks of the free acceptor (PFP) at δ –143.54, –143.58, –143.70, –143.74, –144.46, –144.64, –150.86, –150.91, –150.95, –152.34, and –152.37 ppm. Lowering δ values through CT complex formation is due to the shielding effect of the electron donor on PFP. Although, it has been, also, reported[51] that, no detectable shift in the ^{19}F NMR absorption of the free acceptor and/or donor was found in the ^{19}F NMR spectra of the corresponding CT complex.

Association Constant and Molar Absorption Coefficient of the CT Complex DMAP–PFP

Under the condition [DMAP] >>> [PFP], electronic absorption spectra of CH_2Cl_2 solutions of DMAP as donor with the PFP acceptor were measured. The absorbance values obtained from the CT band at λ_{max} = 401 nm at 20 °C were used for the determination formation constants (K_{CT}) and molar absorption coefficients (ε_{CT}) of the CT complex (DMAP–PFP) using the Benesi–Hildebrand[33] and Scott[34] equations (Eqs (*1*) and (*2*)):

$$[A]_o/A = 1/K_{CT}\,\varepsilon_{CT}\;1/[D]_o + 1/\varepsilon_{CT} \qquad (1)$$

$$[D]_o\,[A]_o/A = 1/K_{CT}\,\varepsilon_{CT} + ([D]_o + [A]_o)/\varepsilon_{CT} - [C]/\varepsilon_{CT} \qquad (2)$$

where A is the absorbance of the CT mixture, $[D]_o$ and $[A]_o$ are the initial concentrations of the donor and acceptor, respectively, and [C] represents the concentration of the CT complex.

The high values of the association constant, K_{CT} = 165.08 (±7.82) $dm^3\ mol^{-1}$ and molar absorption coefficient, ε_{CT} = 1117.6 (±10.5) $dm^3\ mol^{-1}\ cm^{-1}$ of the DMAP–PFP CT complex are consistent with the ionization potential of the donor (IP = 9.8 eV)[18], and they are comparable to those previously reported[52] for cases with strong CT complexation involving *n*-donors.

CONCLUSIONS

Two remarkable cases are presented by this piece of work and each of them undergoes CT at least initially.

Case 1: The acceptor itself can accommodate the unpaired electron pair(s) donated by the donor and, in turn, the acceptor is transformed to a new compound having a clear and definite negative charge, the reduced form. In this case the CT complexation occurs between the donor DMAP and the resulting in situ reduced form of the acceptor as in the case of DMAP with I_2 and with DDQ.

Case 2: The acceptor cannot accommodate the electrons donated by the donor; a quaternary salt of the donor ($DMAPH^+OH^-$) is formed. This quaternary salt is in turn the new donor formed in situ and forming the CT complexes with acceptors as in the case of DMAP with fluorocarbons OFT, OFN, PFP, and TFP.

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REFERENCES

1. Ravishankara A. R., Solomon S., Turnipseed A. A., Warren R. F.: *Science* **1993**, *259*, 194.
2. Molina M. J., Rowland F. S.: *Nature* **1974**, *249*, 810.
3. Anderson R. F., Punderson J. O. in: *Organofluorine Chemicals and Their Industrial Applications* (R. E. Banks, Ed.). Ellis Horwood, Chichester 1979.
4. Chambers R. D.: *Fluorine in Organic Chemistry*. Wiley, New York 1973.
5. Banks R. E., Smart B. E., Tatlow J. C.: *Organofluorine Chemistry. Principles and Commercial Applications*. Plenum Press, New York 1994.
6. Beaumont T. G., Davis K. M. C.: *J. Chem. Soc. B* **1967**, 1131.
7. Boeyens J. C. A., Herbstein F. H.: *J. Phys. Chem.* **1965**, *69*, 2153.
8. Nandel F., Jain D. V. S.: *Indian J. Chem., Sect. A: Inorg., Phys., Theor. Anal.* **1984**, *23*, 543.
9. Dahl T.: *Acta Chem. Scand.* **1989**, *43*, 172.
10. Brown N. M. D., Foster R., Fyfe C. A.: *J. Chem. Soc. B* **1967**, 406.
11. Andrews L. J., Keefer R. M.: *J. Org. Chem.* **1988**, *53*, 537.
12. Mourad A. E.: *Spectrochim. Acta, Part A* **1987**, *43*, 11.
13. Tanaka M.: *Bull. Chem. Soc. Jpn.* **1993**, *66*, 3171.
14. Burdeniuc J., Sanford M., Crabtree R. H.: *J. Fluorine Chem.* **1998**, *91*, 49.
15. Burdeniuc J., Crabtree R. H., Rheingold A. L., Yap G. P. A.: *Bull. Soc. Chim. Fr.* **1997**, *134*, 955.
16. Beck C. M., Burdeniuc J., Crabtree R. H., Rheingold A. L., Yap G. P. A.: *Inorg. Chim. Acta* **1998**, *270*, 559.
17. Yahagi E., Matsumura S., Imai Y., Aida K.: *Spectrochim. Acta, Part A* **1987**, *43*, 711.
18. Daisey J. M., Sonnessa A. J.: *J. Phys. Chem.* **1972**, *76*, 1895.
19. Spivey A. C., Fekner T., Spey S. E.: *J. Org. Chem.* **2000**, *65*, 3154.
20. Ruble J. C., Latham H. A., Fu C. G.: *J. Am. Chem. Soc.* **1997**, *119*, 1492.
21. Ruble J. C., Tweddell J., Fu C. G.: *J. Org. Chem.* **1998**, *63*, 2794.
22. Tao B., Ruble J. C., Hoic D. A., Fu C. G.: *J. Am. Chem. Soc.* **1999**, *121*, 5091.
23. Rabie U. M., Salman H. M. A., Abou-El-Wafa M. H. M.: *Bull. Chem. Soc. Jpn.* **2004**, *77*, 681.
24. Rabie U. M., Patel B. P., Crabtree R. H., Mahmoud M. R.: *Inorg. Chem.* **1997**, *36*, 2236.
25. Matsunaga Y.: *J. Phys. Chem.* **1964**, *41*, 1609.
26. Bhat S. N., Rao C. N. R.: *J. Am. Chem. Soc.* **1966**, *88*, 3216.

27. Brandon R. L., Osiecki J. H., Ottenberg A.: *J. Org. Chem.* **1966**, *31*, 1214.
28. Bhattacharjee B., Varshney A., Bhat S. N.: *J. Indian Chem. Soc.* **1983**, *60*, 842.
29. Muller P., Joly D.: *Helv. Chim. Acta* **1983**, *66*, 1110.
30. Miller J. S., Krusic P. J., Dixon D. A., Reiff W. M., Zhang J. H., Anderson E. C., Epstein A. J.: *J. Am. Chem. Soc.* **1986**, *108*, 4459.
31. Salman H. M. A., Rabie U. M., Abd-Alla E. M.: *Can. J. Anal. Spectrosc.* **2002**, *49*, 1.
32. Salman H. M. A., Mahmoud M. R., Abou-El-Wafa M. H. M., Rabie U. M., Crabtree R. H.: *Inorg. Chem. Commun.* **2004**, *7*, 1209.
33. Benesi H. A., Hildebrand J. H.: *J. Am. Chem. Soc.* **1949**, *71*, 2703.
34. Scott R. L.: *Rec. Trav. Chim. Pays-Bas* **1956**, *75*, 787.
35. Hamed M. M. A., Abdalla E. M., Mahmoud M. R.: *Can. J. Appl. Spectrosc.* **1994**, *39*, 24.
36. Rao N. S., Rao G. B.: *Spectrochim. Acta, Part A* **1990**, *46*, 1107.
37. Hasani M., Shamsipur M.: *J. Inclusion Phenom. Macromol. Chem.* **2004**, *48*, 135.
38. Albert A. in: *Physical Methods in Heterocyclic Chemistry* (A. R. Katritzky, Ed.), Vol. 1. Academic Press, New York 1963.
39. Weisstuch A., Testa A. C.: *J. Phys. Chem.* **1970**, *74*, 2299.
40. Lambert J. B., Shurvell H. F., Lightner D. A., Cooks R. G.: *Introduction to Organic Spectroscopy*. Macmillan Publishing Company, New York 1987.
41. Gebert E., Reis A. H., Jr., Miller J. S., Rommelmann H., Epstein A. J.: *J. Am. Chem. Soc.* **1982**, *104*, 4403.
42. Zanotti G., Pra A. D.: *J. Am. Chem. Soc.* **1982**, *38*, 1225.
43. El-Gyar S. A., El-Nady A. M., Salman H. M. A.: *Bull. Soc. Chim. Fr.* **1990**, *127*, 485.
44. Mahmoud M. M., Hamed M. M. A., Salman H. M. A.: *Spectrochim. Acta* **1988**, *44*, 1185.
45. Hamed M. M. A., Bakr M., Mahmoud M. R.: *Spectrosc. Lett.* **1995**, *28*, 29.
46. Iida Y.: *Bull. Chem. Soc. Jpn.* **1971**, *44*, 2615.
47. Iida Y., Matsunga Y.: *Bull. Chem. Soc. Jpn.* **1967**, *40*, 231.
48. Miller J. S., Epstein A. J., Reiff W. M.: *Chem. Rev.* **1988**, *88*, 201.
49. Alkorta I., Rozas I., Elguero J.: *J. Org. Chem.* **1997**, *62*, 4687.
50. Lide D. R.: *Handbook of Chemistry and Physics*, 77th ed. CRC Press, New York 1996–1997.
51. Foster R., Fyfe C. A.: *Chem. Commun.* **1965**, 642.
52. Foster R.: *Organic Charge-Transfer Complexes*. Academic Press, London 1969.