

Solid-State Charge Transfer Promoted by an Anchoring Agent: A Two-Component Analogue of Kofler's Ternary Complex

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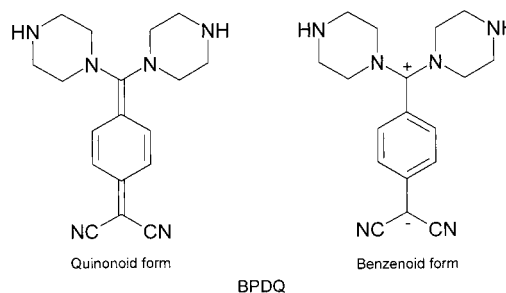
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Charge-transfer complex formation between the push–pull zwitterionic molecule 7,7-bis(piperazino)-8,8-dicyanoquinodimethane and picric acid is observed in the solid state. The critical role of proton transfer and intermolecular H bonding in facilitating the charge-transfer interaction is established through control experiments and single-crystal X-ray investigation of the complex. The details of the π – π interaction are analyzed using computed atomic charges.

Introduction

A classic example of a versatile electron acceptor molecule for charge-transfer (CT) complexes is picric acid. It forms colored CT complexes with a wide variety of donor molecules and has proved useful in qualitative and quantitative analysis protocols.¹ A very large number of complexes of picric acid have been characterized crystallographically; a survey of the recent update of the Cambridge Crystallographic Database² shows 280 hits for purely organic complexes alone. While the majority of CT complexes of picric acid are yellow, several complexes are known to be red to deep red, indicating a lower CT energy. A cursory examination of the red CT complexes reveals an interesting phenomenon; the picric acid exists in the neutral form in some systems, whereas in the others it is deprotonated to form the picrate ion. In the complexes where picric acid is in the neutral form, the lower CT energy usually arises because of the strong donor molecules present.^{3–7} However, an early example of a red complex, the Kofler's ternary complex consisting of naphthylamine, pyridine, and picric acid,^{8,9} is a curious case. Spectroscopic and crystallographic studies suggest that the color is due to CT from naphthylamine to the picrate ion.^{9–11} Though

counterintuitive, based on spectroscopic experiments,^{9,10} it has been suggested that the picrate ion is as good an acceptor as picric acid. Further it appears that proton transfer between picric acid and pyridine is crucial for the formation of the red complex; we believe that pyridine plays the role of an *anchoring agent* in facilitating CT between the weak donor and the picrate ion. Such a phenomenon may have wider generality. For example, consider the "picrate effect" demonstrated in the extraction selectivities of aromatic group-containing crown ethers for alkali-metal cations.¹² This is a consequence of the π – π interaction between the aromatic moiety and picrate ion and its influence on the binding of the metal ion by the crown ether. This can be visualized as the inverse phenomenon to the anchoring of the picrate by the alkali-metal ions.



We have been investigating the quadratic nonlinear optical properties of diaminodicyanoquinodimethanes;¹³ these molecules exist in strongly zwitterionic benzenoid form. Recently, we observed an unexpected red complex formation between the zwitterionic push–pull molecule

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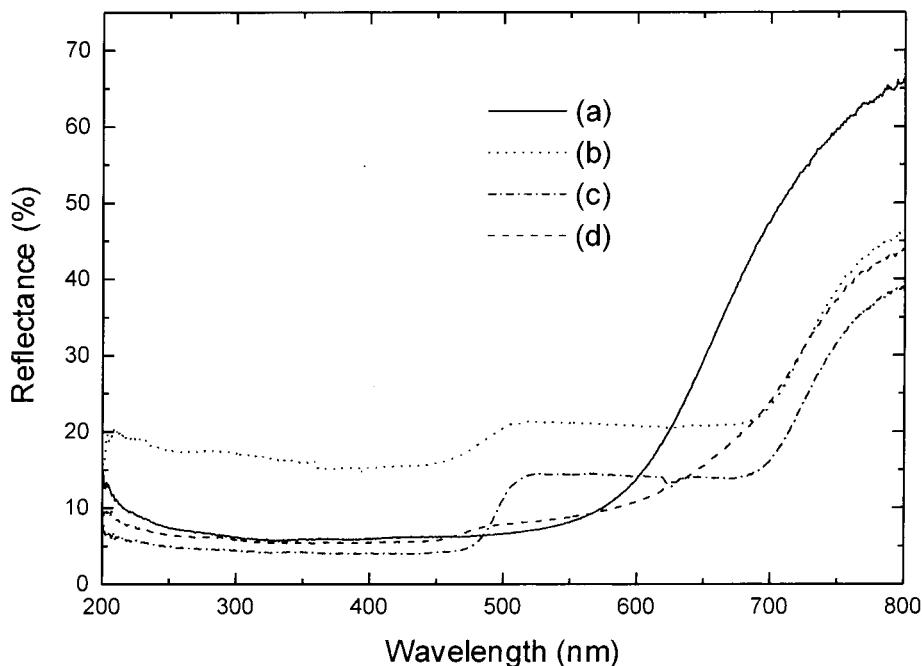


Figure 1. Diffuse reflectance spectra of (a) $\text{BPDQH}_2^{2+}(\text{Pic}^-)_2$, (b) naphthalene–PicH, (c) piperazinium picrate, and (d) BDEDQ–PicH.

7,7-bis(piperazino)-8,8-dicyanoquinodimethane (BPDQ) and picric acid (PicH); the complexation occurs exclusively in the solid state. We report in this paper detailed crystallographic characterization of this material and several control experiments which show that the complex formed between BPDQ and PicH is a two-component analogue of Kofler's ternary complex. The secondary amine moiety of the piperazine units in BPDQ molecules plays the role of anchoring agents, and the electron-rich dicyanomethylene end of the zwitterions participates in CT with the picrate ions. Computational studies support the earlier suggestions regarding the electron-accepting capability of the picrate ion and provide insight into the nature of the CT interaction.

The complex of BPDQ with picric acid presents a graphic case of intermolecular CT facilitated by molecular anchoring. The amine end of BPDQ carries out the function of a trigger by helping set up the suitable juxtapositioning of the molecules to facilitate CT. CT from the dicyanomethylene end of BPDQ to the picrate ion can be visualized as a response. Thus, BPDQ operates as a novel molecular device wherein CT is triggered by remote intermolecular interactions.

Experimental and Computational Section

BPDQ was synthesized following the procedure reported earlier.^{14,15} The crystal structure of BPDQ has also been reported in ref 15. The complex with PicH was prepared by mixing saturated acetonitrile solutions of 0.10 g (0.31 mmol) of BPDQ and 0.14 g (0.62 mmol) of PicH. The complex precipitated out as a reddish brown microcrystalline powder. Single crystals were grown by a diffusion process. BPDQ and PicH were taken as acetonitrile solutions in the two limbs of an inverted Y tube, and contact between the solutions was established by careful addition of the solvent. Deep red crystals appeared at the confluence of the two limbs in 3–4 days.

Electronic absorption and diffuse reflectance spectra were recorded on a Shimadzu UV–vis–NIR scanning spectrophotometer (model UV-3101PC) using appropriate absorption/reflectance sample assemblies. Electronic absorption spectra

were recorded in an acetonitrile solution. For the reflectance spectra, samples were mixed in a 1:100 weight ratio with KBr and pressed into pellets. A BaSO_4 pellet was used as the white standard.

X-ray diffraction data were collected on an Enraf-Nonius MACH3 diffractometer. $\text{Mo K}\alpha$ radiation with a graphite crystal monochromator in the incident beam was used. Data were reduced using Xtal3.4,^{16a} Lorentz and polarization corrections were included. All non-hydrogen atoms were found using the direct method analysis in SHELX-97,^{16b} and after several cycles of refinement, the positions of the hydrogen atoms were calculated and added to the refinement process. Graphics were handled using ORTEP6a.^{16c} Details of data collection, solution, and refinement, fractional coordinates with anisotropic thermal parameters, and full lists of bond lengths and angles are submitted as Supporting Information.

Charge densities on the bisprotonated BPDQ (BPDQH_2^{2+}) and picrate ion (Pic^-) were estimated using ab initio calculations at the B3LYP/6-31G* level.^{17a} The calculations employed molecular geometries from the crystal structure analysis; H atom positions alone were optimized. The polar environment around molecules in crystals can be mimicked satisfactorily using solvation models built into quantum chemical programs.^{18,19} Our recent study of push–pull quinonoids¹⁹ as well as earlier computations by Jiao and Schleyer on donor–

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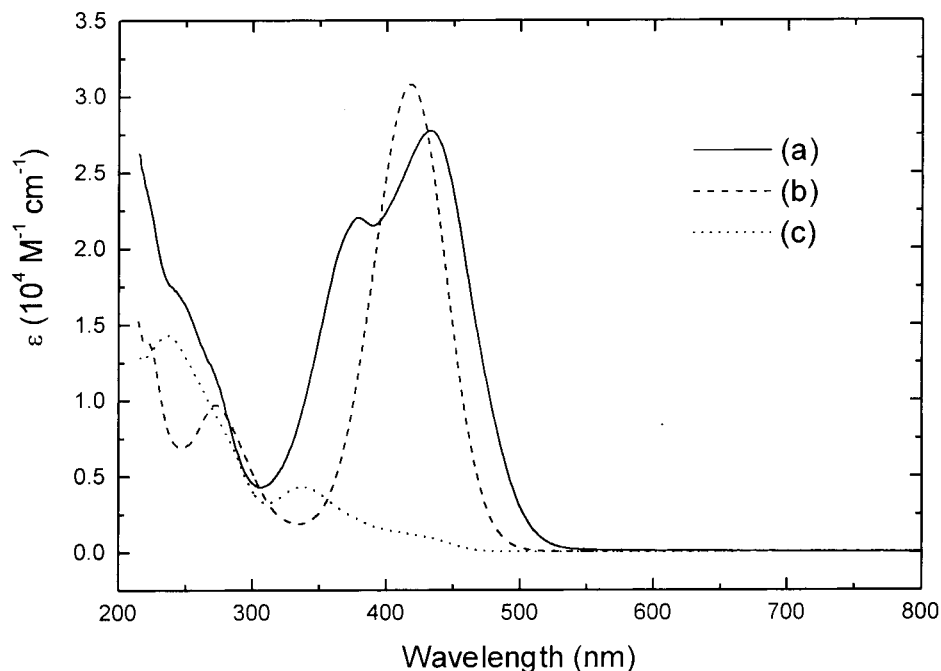


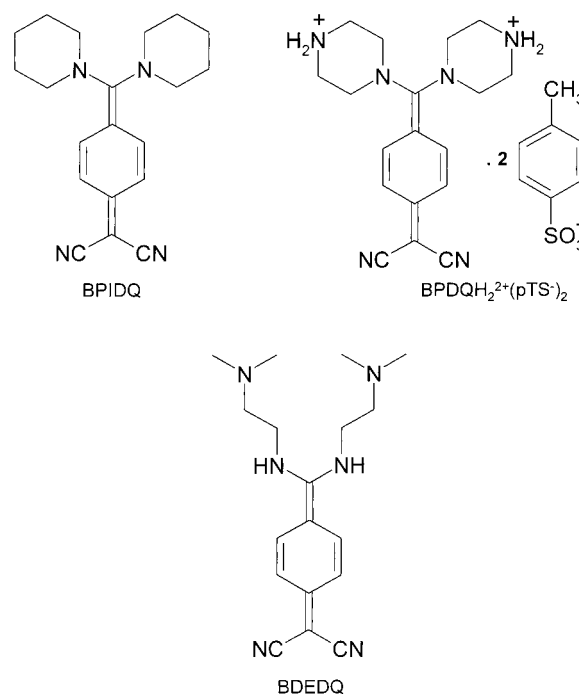
Figure 2. Electronic absorption spectra of an acetonitrile solution of (a) $\text{BPDQH}_2^{2+}(\text{Pic}^-)_2$, (b) BPDQ, and (c) PicH.

acceptor complexes¹⁸ have shown that critical geometric parameters in the crystalline state can be reproduced satisfactorily by incorporating an $\epsilon > 10$ –20. In the current study we have used the polarized continuum model^{17b,c} for solvation with acetonitrile as the solvent ($\epsilon = 36.64$) to mimic the crystalline environment and obtain a realistic picture of the charge polarization in the ions.

Results and Discussion

BPDQ is a yellow solid and forms a yellow solution in acetonitrile. When this solution is mixed with a solution of picric acid in acetonitrile in a 1:2 mole ratio, a reddish brown microcrystalline precipitate forms immediately. The complex can be prepared by grinding together BPDQ and PicH in the solid state as well. The diffuse reflectance spectrum of the solid is presented in Figure 1. The figure shows also the spectrum of the well-known yellow naphthalene picrate for comparison. The red color of the complex of BPDQ with PicH is indicative of a low-energy CT. When the complex is dissolved in excess acetonitrile as well as other polar solvents such as water, methanol, and dimethyl sulfoxide, a yellow solution is obtained. The red complex can be retrieved by slow evaporation of the solution. Electronic absorption spectra of acetonitrile solutions of BPDQ, PicH, and the complex are shown in Figure 2. The peaks at 246 and 379 nm in the spectrum of the complex are signatures of the picrate ion (the acetonitrile solution of sodium picrate shows peaks at 248 and 376 nm), and the peak at 432 nm is similar to that seen for $\text{BPDQH}_2^{2+}(\text{pTS}^-)_2$ and hence can be assigned to BPDQH_2^{2+} . No CT band is visible, and this spectrum shows that the complex exists as BPDQH_2^{2+} and Pic^- ions in solution. From the solution study and the reflectance spectrum of the solid, we conclude that the dark red complex exists only in the solid state. Because BPDQ is known to be in a strongly zwitterionic state,¹⁵ the formation of a CT complex with picric acid, especially in the picrate form, is surprising. To gain insight

into the phenomenon, we have prepared several control systems.



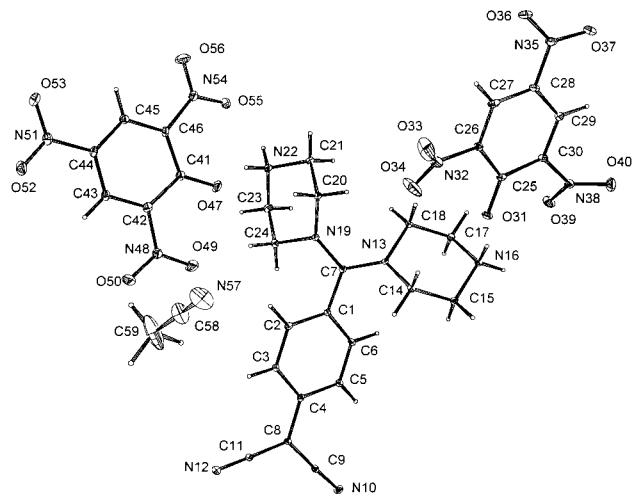
Piperazine forms a yellow salt with picric acid. Despite several attempts, we found that 7,7-bis(piperidino)-8,8-dicyanoquinodimethane (BPIDQ) does not form a complex with picric acid. The observation when the *p*-toluenesulfonate salt of BPDQ, i.e., $\text{BPDQH}_2^{2+}(\text{pTS}^-)_2$, was mixed with picric acid was similar. However, a dark reddish brown precipitate was obtained when 7,7-bis(*N,N*-dimethylethylenediamine)-8,8-dicyanoquinodimethane (BDEDQ) was mixed with picric acid. Diffuse reflectance spectra of piperazinium picrate and BDEDQ–PicH complexes are presented in Figure 1. These studies clearly indicate the significant role of the

Table 1. Crystallographic Data for BPDQH₂²⁺(Pic⁻)₂-CH₃CN

molecular formula	C ₃₂ H ₃₁ N ₁₃ O ₁₄
formula weight	821.70
crystal system	monoclinic
space group	<i>P</i> $\bar{1}$
<i>a</i> , Å	10.198(5)
<i>b</i> , Å	12.177(3)
<i>c</i> , Å	16.041(9)
α , deg	89.12(3)
β , deg	72.99(3)
γ , deg	75.40(3)
<i>Z</i>	2
ρ_{calc} , g cm ⁻³	1.483
μ , cm ⁻¹	1.19
no. of unique reflections	7191
no. of reflections with $I \geq \sigma_1$	4759
no. of parameters	533
GOF	1.062
<i>R</i> (for $I \geq 2\sigma_1$)	0.0669
<i>wR</i> ²	0.1931

free amine moieties (which are not in conjugation with the zwitterionic system and, hence, are strongly basic) and the delocalized π -electron system in BPDQ in the formation of the dark colored complex with picric acid; similar functionalities are present in BDEDQ as well. The fact that neither functionality alone is sufficient is proven by the color of the piperazinium picrate and the failure of BPIDQ to complex PicH. It is also observed that BPDQH₂²⁺, which is already engaged by a counterion such as pTS⁻, cannot produce the colored CT complex with picric acid. We conclude tentatively that the secondary amine moiety in BPDQ helps to anchor the picric acid through proton transfer and/or H bonding, facilitating CT interaction with the zwitterionic π system. In an effort to understand the role of the zwitterionic π system, we have explored some further complexation reactions. BPDQ forms dark green/brown complexes with well-known electron acceptors such as 7,7,8,8-tetracyanoquinodimethane, tetracyanoethylene, and 2,3-dichloro-5,6-dicyano-1,4-benzoquinone and even with weaker acceptors such as chloranil. It, however, does not produce any characteristic color of CT complexes when mixed with electron donors such as tetrathiafulvalene and *N,N,N,N*-tetramethyl-1,4-phenylenediamine. Therefore, the zwitterionic π system appears to be effective only as an electron donor, implying that the negative end alone participates in any CT process.

A detailed picture of the interactions in the solid state is provided by single-crystal X-ray analysis of the complex of BPDQ with PicH. Single crystals were grown as deep red rhombus-shaped plates by the diffusion process in acetonitrile; they are found to belong to the triclinic space group, *P* $\bar{1}$. The crystallographic data are presented in Table 1. The asymmetric unit consists of one bisprotonated ion, BPDQH₂²⁺, two Pic⁻ ions, and one molecule of acetonitrile (Figure 3). The significant bond lengths and angles are collected in Table 2. The C–O bond length in the picric acid molecules, 1.241 and 1.244 Å (compare with the average value of 1.236 Å for picrate ion^{20a,b} and 1.324 Å for picric acid^{20b,c}), as well as the C–N bond lengths around the secondary amine moiety in the piperazine units of BPDQ, 1.476, 1.480, 1.486, and 1.489 Å (compare with the average value of

**Figure 3.** Molecular structure of BPDQH₂²⁺(Pic⁻)₂-CH₃CN from single-crystal X-ray diffraction analysis. 5% probability thermal ellipsoids are shown.**Table 2. Significant (a) Bond Lengths and (b) Bond Angles in BPDQH₂²⁺(Pic⁻)₂-CH₃CN**

(a) Bond Lengths			
bond	length (Å)	bond	length (Å)
N10–C9	1.139(6)	C4–C8	1.436(6)
N12–C11	1.152(6)	C5–C6	1.370(6)
N13–C7	1.332(6)	C8–C11	1.393(7)
N16–C15	1.480(6)	C8–C9	1.406(7)
N16–C17	1.489(6)	C25–C26	1.425(7)
N19–C7	1.339(6)	C25–C30	1.431(7)
N22–C21	1.486(6)	C26–C27	1.363(7)
N22–C23	1.476(7)	C27–C28	1.362(8)
O31–C25	1.244(5)	C28–C29	1.369(8)
O47–C41	1.241(7)	C29–C30	1.352(7)
C1–C2	1.383(6)	C41–C46	1.429(8)
C1–C6	1.386(7)	C41–C42	1.462(8)
C1–C7	1.446(6)	C42–C43	1.369(8)
C2–C3	1.366(6)	C43–C44	1.369(8)
C3–C4	1.396(6)	C44–C45	1.366(7)
C4–C5	1.415(7)	C45–C46	1.361(7)

(b) Bond Angles			
bond–bond	angle (deg)	bond–bond	angle (deg)
C15–N16–C17	110.9(4)	C5–C4–C8	120.6(4)
C23–N22–C21	110.2(4)	C6–C5–C4	120.7(5)
C7–N13–C14	122.2(4)	C5–C6–C1	121.3(5)
C7–N13–C18	124.9(4)	N13–C7–N19	120.2(4)
C14–N13–C18	112.5(4)	N13–C7–C1	119.1(4)
C7–N19–C20	124.0(4)	N19–C7–C1	120.6(4)
C7–N19–C24	121.9(4)	C11–C8–C9	118.5(4)
C20–N19–C24	112.7(4)	C11–C8–C4	122.1(4)
C2–C1–C6	118.0(4)	C9–C8–C4	119.3(4)
C2–C1–C7	122.4(4)	O31–C25–C26	123.8(5)
C6–C1–C7	119.6(4)	O31–C25–C30	124.8(5)
C3–C2–C1	121.8(5)	C26–C25–C30	111.3(4)
C2–C3–C4	121.0(5)	O47–C41–C46	125.3(5)
C3–C4–C5	117.2(4)	O47–C41–C42	122.4(6)
C3–C4–C8	122.2(5)	C46–C41–C42	112.3(5)

1.483 Å in BPDQH₂²⁺(pTS⁻)₂¹⁹ and 1.451 Å in BPDQ¹⁵), clearly indicate the proton transfer from picric acid to BPDQ in the solid complex. Further, a careful search of the difference Fourier map did not reveal any H atom bonded to the phenolate O atom on the picric acid molecules. The bond lengths in BPDQH₂²⁺ indicate clearly the benzenoid structure of the zwitterionic system. Examination of the crystal packing revealed four well-defined intermolecular H-bond contacts around the BPDQH₂²⁺ ion. The piperazinium moieties form H

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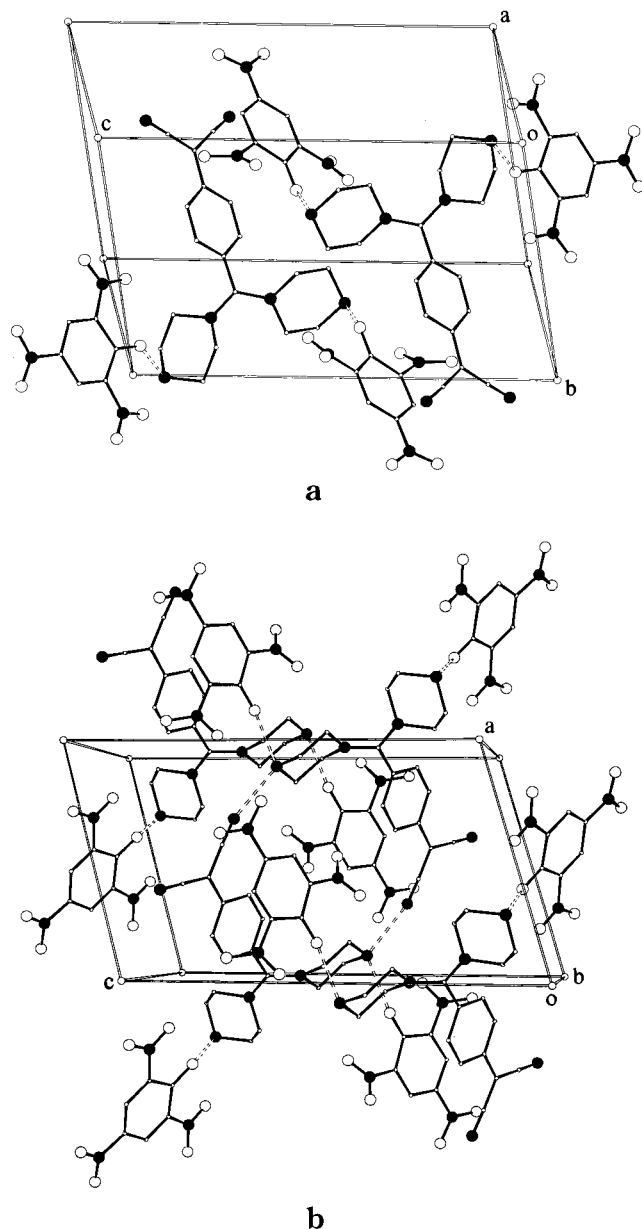


Figure 4. (a) Molecules in the unit cell and (b) unit cell packing along the *b* axis of $\text{BPDQH}_2^{2+}(\text{Pic}^-)_2$. C (○), N (●), and O (○) atoms and H bonds (— — —) are indicated; all H atoms and the solvent molecule of acetonitrile are omitted for clarity.

bonds with the picrate ions: N16—O31 ($\text{H16B}\cdots\text{O31} = 1.821 \text{ \AA}$ and $\text{N16}-\text{H16B}\cdots\text{O31} = 163.9^\circ$) and N22—O47 ($\text{H22A}\cdots\text{O47} = 1.913 \text{ \AA}$ and $\text{N22}-\text{H22A}\cdots\text{O47} = 152.8^\circ$). The second piperazinium unit forms an additional H bond with one of the O atoms of an ortho nitro group of the picric acid: N22—O55 ($\text{H22B}\cdots\text{O55} = 2.132 \text{ \AA}$ and $\text{N22}-\text{H22B}\cdots\text{O55} = 160.9^\circ$). The fourth H bond is found between the first piperazinium moiety and one of the cyano N atoms of BPDQ: N16—N10 ($\text{H16A}\cdots\text{N10} = 1.920 \text{ \AA}$ and $\text{N16}-\text{H16A}\cdots\text{N10} = 168.1^\circ$). These H bonds, especially the first three, appear to play a critical role in sequestering the picrate ions into appropriate positions which enables CT interactions with BPDQH_2^{2+} ions. Figure 4a shows the molecular packing in the unit cell of $\text{BPDQH}_2^{2+}(\text{Pic}^-)_2$. It is seen that the dicyanomethylene unit of one BPDQH_2^{2+} has close $\pi-\pi$ contact with the picrate ion anchored by the

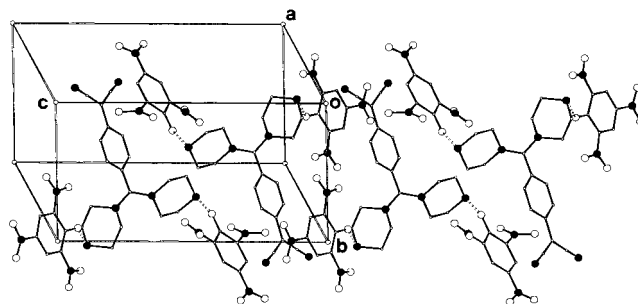


Figure 5. Unit cell packing along the *c* axis of $\text{BPDQH}_2^{2+}(\text{Pic}^-)_2$. C (○), N (●), and O (○) atoms and H bonds (— — —) are indicated; all H atoms and the solvent molecule of acetonitrile are omitted for clarity.

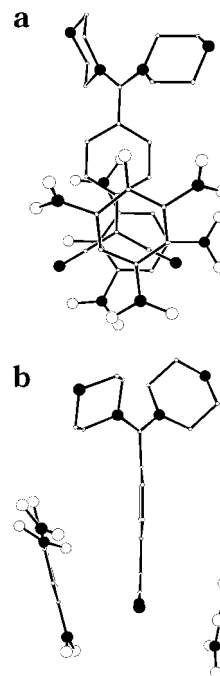


Figure 6. View of the overlap of the BPDQH_2^{2+} ion with the adjacent picrate ions approximately (a) perpendicular and (b) parallel to the mean molecular planes. C (○), N (●), and O (○) atoms are indicated.

other BPDQH_2^{2+} . A view along the *b* axis (Figure 4b) shows, in addition, the H bond between the piperazinium unit and the cyano group of the neighboring BPDQH_2^{2+} , leading to a dimer motif. The packing along the *c* axis shown in Figure 5 reveals the close $\pi-\pi$ contact of a second picrate ion to the dicyanomethylene unit of BPDQH_2^{2+} . It is thus seen that each BPDQH_2^{2+} has close interaction with two picrate ions on either side and at the same time anchors two other picrate ions through H-bonding interactions, facilitating, in turn, their $\pi-\pi$ interaction with other BPDQH_2^{2+} . The stacking of the dicyanomethylene unit of BPDQH_2^{2+} and the two picrate ions is shown clearly in Figure 6. We define least-squares planes A, B, and C based on the dicyanomethylene unit (C8, C9, N10, C11, and N12), the ring atoms of the first picrate ion (C25–C30), and the ring atoms of the second picrate ion (C41–C46), respectively. The angle between planes A and B is 16.9° , and the average distance of the atoms in plane A from the mean plane B is 3.090 \AA . Similarly, the angle between planes A and C is 6.3° , and the average distance of the atoms in plane A from the mean plane C is 3.220 \AA . This is

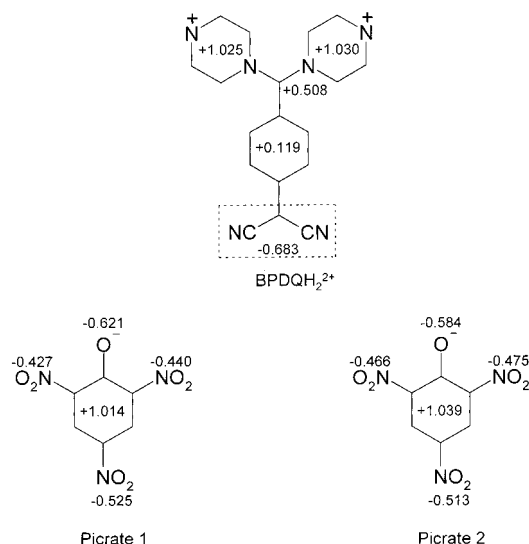


Figure 7. Computed net atomic charges in different parts of BPDQH₂²⁺ and Pic⁻ ions (see text for details).

highly suggestive of the existence of strong π - π interaction between the dicyanomethylene unit and the picrate ion rings which should facilitate CT.

We have examined this aspect by calculating the atomic charges on the BPDQH₂²⁺ and Pic⁻ ions using the molecular geometry from crystal structure analysis as described earlier. The net charges possessed by different parts of these ions revealed through ab initio calculations are shown in Figure 7. In BPDQH₂²⁺ the dicyanomethylene unit possesses considerable negative charge and is a potential π -electron donor moiety; it is also obvious that this ion cannot act as a π -electron acceptor because of the steric bulk and nonplanar structure at the positive end. The picrate ions interestingly reveal a full-fledged positive charge in the ring surrounded by approximately a -2 charge accommodated in the phenolate and nitro groups. This clearly establishes the π -electron-accepting capability of the picrate ion suggested earlier.⁹ The distribution of the

calculated charges also strongly supports the possibility of π - π CT interaction in the configuration shown in Figure 6.

Conclusion

We have observed a controlled CT complexation between push-pull zwitterionic molecules and picric acid. CT occurs only in the solid state and requires the anchoring of the picric acid in the form of picrate ion by a remote amine functionality in the push-pull molecule. This picture is elaborated using the crystal structure analysis of BPDQH₂²⁺(Pic⁻)₂. The π - π interaction between the dicyanomethylene moiety of BPDQH₂²⁺ and the picrate ion and its facilitation by the H bonding of the picrate ion to the piperazinium moiety are revealed. The mode of CT interaction is demonstrated using computed atomic charges on the respective ions.

The mechanism of induction of CT presented in this study also provides insight into the role of pyridine as an anchoring agent in Kofler's ternary complex and other amine picrates. The picrate effect noted earlier¹² is in a general sense a similar phenomenon and is of interest in analytical applications. Further investigations are required to shed more light on the generality and utility of anchoring agent-mediated CT materials.

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Supporting Information Available: X-ray structure determination and crystal structure details and detailed computational results (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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