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# Comparison of Photoelectron Transfer in Solution and the Solid State for Two Intervalence Radical Cations

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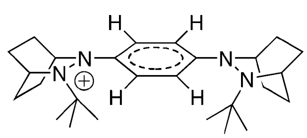
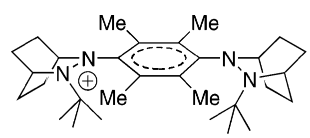
## ABSTRACT



**$Hy_2PH^+$**



**$Hy_2DU^+$**

**The optical diffuse reflectance and solution spectra of two bis-hydrazine radical cationic intervalence compounds have been compared. The results are consistent with an ion-pairing increase and an "effective polarity" in these crystals that is not far from that of acetonitrile or other polar solvents.**

Localized "symmetrical" intervalence compounds have two charge-bearing units (**M**) connected by a bridge (**B**), and charge is almost localized on one **M** unit, so they are $\mathbf{M^+BM} \leftrightarrow \mathbf{MBM^+}$ electron-transfer systems. According to Marcus−Hush two-state theory,[1] the transition energy for their lowest energy optical absorption band is the vertical reorganization energy ($\lambda$), and the electronic coupling through the bridge between the **M** units ($H_{ab}$) may also be evaluated from this optical band if the electron transfer distance is known. The importance of medium effects on charge-transfer, often studied most conveniently within intervalence compounds, has long been emphasized.[2] Nelsen and co-workers have shown that simple classical Marcus−Hush theory predicts the electron-transfer barrier measured by ESR surprisingly well for several hydrazine- and diazene-centered radical cationic intervalence compounds,[3] so these parameters evaluated in this way for the compounds considered here have experimental significance. Most localized intervalence salts cannot be isolated as solids because electron-transfer disproportionation to neutral and dication mixtures occurs upon attempted crystallization, but choosing counterions about the same size as the intervalence ion minimizes this problem. Disproportionation was still found to occur for analogous compounds with smaller $H_{ab}$, but both the *p*-phenylene and *p*-durenylene-bridged bis-hydrazine radical cation salts $\mathbf{Hy_2PH^+Ph_4B^-}$ and $\mathbf{Hy_2DU^+Ph_4B^-}$ were isolated and have had their X-ray structures determined,[4] making them uniquely available for solid-state studies of their optical spectra, which allows comparison of the vertical reorganization energies of their crystals to solutions containing them. Their diffuse reflectance spectra show intervalence band maxima at 15900 and 15100 cm$^{-1}$, respectively, using $Al_2O_3$ as the solid-state support (see Figure 1).

Comparison of the spectrum in acetonitrile solution (at 298 K)[5] with that of the solid salt $\mathbf{Hy_2DU^+}Ph_4B^-$ on alumina

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(1) For basic classical Marcus−Hush theory, see: (a) Marcus, R. A.; Sutin, N. *Biochim. Biophys. Acta* **1985**, *811*, 265. (b) Hush, N. S. *Coord. Chem. Rev.* **1985**, *64*, 135.
(2) Chen, P.; Meyer, T. J. *Chem. Rev.* **1998**, *98*, 1439.
(3) Nelsen, S. F.; Ismagilov, R. F.; Trieber, D. A., II. *Science* **1997**, *278*, 846.
(4) Nelsen, S. F.; Ismagilov, R. F.; Powell, D. R. *J. Am. Chem. Soc.* **1997**, *119*, 10213.
(5) Nelsen, S. F.; Ismagilov, R. F.; Gentile, K. E.; Powell, D. R. *J. Am. Chem. Soc.* **1999**, *121*, 7108.

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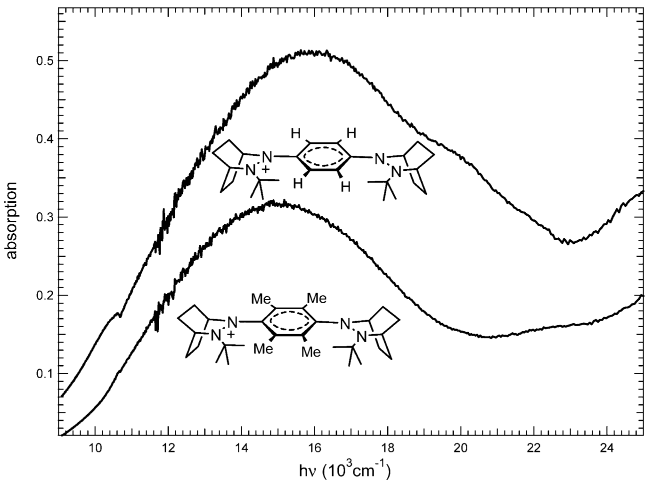


**Figure 1.** Comparison of diffusion reflectance spectra of **Hy$_2$PH$^+$** and **Hy$_2$DU$^+$** on $Al_2O_3$.

(Figure 2) shows that the intervalence band shapes are very similar, and that there is an increase in $\lambda$ for the solid of

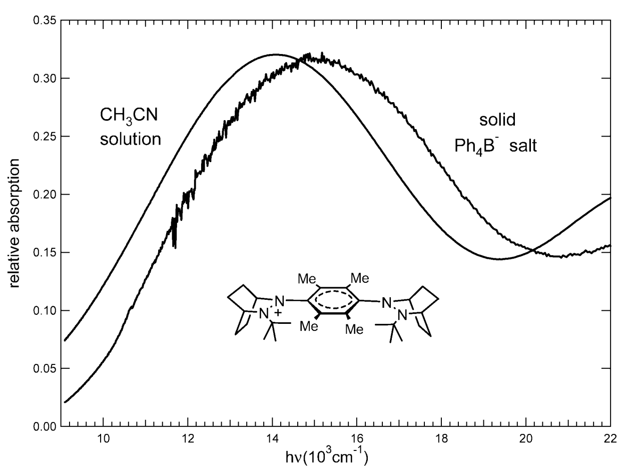


**Figure 2.** Comparison of the acetonitrile solution and the solid $Ph_4B^-$ salt on $Al_2O_3$ optical spectra of **Hy$_2$DU$^+$**.

about 900 cm$^{-1}$. Rate constants for electron transfer between the **Hy** units of **Hy$_2$DU$^+$** in acetonitrile have been measured by ESR between 236 and 265 K, and extrapolated to $8.1 \times 10^8$ s$^{-1}$ at room temperature (298 K), corresponding to a half-life for electron transfer of 0.86 ns.[4] Despite the rather small increase in vertical reorganization energy, intramolecular electron transfer will not occur in the solid because the geometry reorganization and counterion movement that would be required to achieve it cannot occur. Table 1 summarizes ion pairing[6] and solvent effect[7] studies on $\lambda$ for **Hy$_2$DU$^+$**.

(6) Nelsen, S. F.; Ismagilov, R. F. *J. Phys. Chem. A* **1999**, *103*, 5373.
(7) Nelsen, S. F.; Trieber, D. A., II; Ismagilov, R. F.; Teki, Y. *J. Am. Chem. Soc.* **2001**, *123*, 5684.

**Table 1.** Transition Energies from Absorption Maxima (cm$^{-1}$) for **Hy$_2$DU$^+$**

| solvent | maximum (cm$^{-1}$) |
|---|---|
| $CH_2Cl_2$ (free ion) | 12 400[a] |
| $CH_2Cl_2$ (1 mM) | 12 600[b] |
| $CH_2Cl_2$ ($PF_6^-$ ion paired) | 13 100[a] |
| $CH_3CH_2CH_2CN$ | 14 000[c] |
| $CH_3CN$ | 14 100[c] |
| $Me_2C(=O)$ | 14 400[c] |
| DMF ($Me_2NC(=O)H$) | 14 700[c] |
| DMSO ($Me_2S(=O)$) | 14 700[c] |
| solid **Hy$_2$DU$^+$Ph$_4$B$^-$** | 15 100[d] |

[a] Reference 6. [b] Reference 4. [c] Reference 7. [d] $Al_2O_3$ support.

There is an increase of 700 cm$^{-1}$ between the free ion and $PF_6^-$ ion pair in methylene chloride, and the mixture of free ion and ion-paired species observed at 1 mM has a maximum 200 cm$^{-1}$ higher than that of the free ion. The maximum shifts to higher energy in more polar solvents, where the solvent reorganization energy ($\lambda_s$) is expected to be higher. We did not find ion pairing in acetonitrile, and ion pairing is not expected to lead to significant band maximum shifts at the ∼1 mM concentrations studied in any of the more polar solvents. There is a definite shift to higher energy in the more electron-pair donating solvents DMF and DMSO.[7] The solid has a maximum only 300 cm$^{-1}$ higher in energy than these solutions and 900 cm$^{-1}$ higher than acetonitrile solution.

We have looked far less at solvent effects on the rather less stable **Hy$_2$PH$^+$**, but the solid has its maximum 2900 cm$^{-1}$ higher than the 13 000 cm$^{-1}$ observed in acetonitrile solution, about three times larger than the increase observed for **Hy$_2$DU$^+$**, so the band maximum in the solid is 900 cm$^{-1}$ larger for **Hy$_2$PH$^+$** than for **Hy$_2$DU$^+$**, although the band maximum is 1500 and 1800 cm$^{-1}$ smaller in acetonitrile and methylene chloride solutions, respectively. Diffuse reflectance samples are obtained by gently grinding the intervalence bis-hydrazine radical cation salts with a solid support. The identity of the support has a modest influence upon the transition energy, (total range, 400 cm$^{-1}$) as shown in Table 2 and Figure 3. All the solid transition energies are higher

**Table 2.** Transition Energies from Absorption Maxima (cm$^{-1}$) for **Hy$_2$DU$^+$** on Various Supports

| support | maximum (cm$^{-1}$) |
|---|---|
| $Al_2O_3$ | 15 100 |
| LiCl | 15 250 |
| $BaSO_4$ | 15 400, 15 450[a] |
| KBr | 15 600 |

[a] Run at high and low concentrations of **Hy$_2$DU$^+$**.

than any of the solution ones, and alumina gives the smallest value of the supports examined. We are unable to comment on the origin of the relatively small effect of changing support

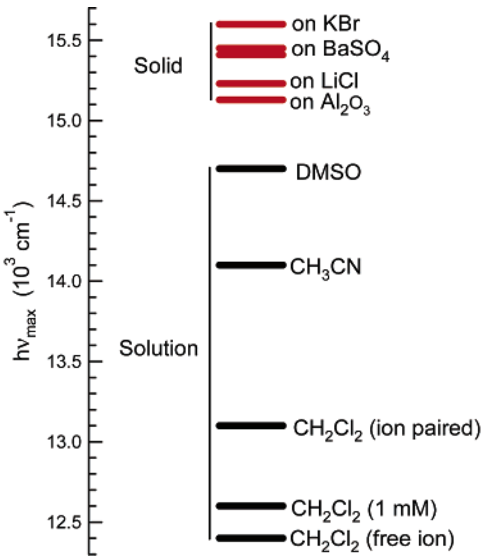


**Figure 3.** Band maxima for **Hy$_2$DU**$^+$Ph$_4$B$^-$ in solution and on solid supports.

but suggest that the crystal structures show why the effect of going from solution to solid is larger for **Hy$_2$PH**$^+$ than for **Hy$_2$DU**$^+$(see Figure 4). The BPh$_4$$^-$ anion is both closer to the oxidized NN bond (B, NN$^+$ midpoint distance 7.41 Å for **Hy$_2$DU**$^+$ and 7.01 Å for **Hy$_2$PH**$^+$) and less symmetrically placed (B, NN$^0$ midpoint distance 6.95−7.24 for the three diasteromers at the neutral NN present in **Hy$_2$DU**$^+$, 10.76 for **Hy$_2$PH**$^+$). We pointed out earlier from solution studies that the size of the ion-pairing effect increases as the counterion becomes less symmetrically placed.[6]

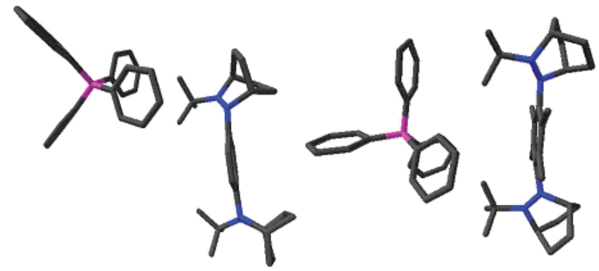

**Figure 4.** Comparison of Ph$_4$B$^-$ counterion placement in crystals of **Hy2PH**$^+$ (left) and **Hy2DU**$^+$ (right).

Our results[8] are quite consistent with an ion pairing increase and an "effective polarity" in these crystals that is not far from that of acetonitrile or other polar solvents.

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(8) **Experimental Procedures.** A 3 mg portion of each salt[4] was added to 220 mg of neutral alumina (Brockman Activity 1; 80−200 mesh) used as inert support and then intimately mixed with a mortar and pestle. The sample was then loaded into a 3 mm quartz cell and the spectrum taken on a Perkin-Elmer Lambda 9 instrument equipped with an integrating sphere. Background correction was carried out by recording the spectrum of the inert support in the same cell. The recorded reflectance spectrum for the sample was subjected to Kubelka−Munk transformation using the Perkin-Elmer software. Duplicate determinations on different days gave the maximum within ±50 cm$^{-1}$. KBr (Spectra Technol. 99+%) was used as purchased, LiCl (Aldrich, 99%) was ground in a mortar and pestle before being dried at 70 °C under a 10$^{-4}$ Torr vacuum for 6 h, and BaSO$_4$ (Spectrum 99.5%) was dried in the same manner as LiCl. For each sample, 190−195 mg of the respective salt was first used in the background correction and subsequently mixed with 3.4−3.5 mg of **Hy$_2$DU**$^+$(BPh$_4$$^-$), by first mixing using a metal spatula and then lightly grinding using a mortar and pestle. Particle size affects the effective signal intensity. The BaSO$_4$ sample tended to clump up and gave a weak spectrum, so a second was determined using 7 mg of **Hy$_2$DU**$^+$ (BPh$_4$$^-$), resulting in the same maximum within ±25 cm$^{-1}$.