erably lower information content concerning bonding than does an electron-density plot. We believe that a measurement of the axial slope and intensity of the electron density in the center of the bond axis, as well as some measure of the diffuseness of the electrons at right angles to the bond axis at its center, coupled with an indication of how many electrons are involved in the pillar of unshared valence-orbital charge held close to the nucleus, will give a set of four parameters whereby chemical bonds can be readily intercompared (within a given group of basis sets). Further examples of related molecules based on different atoms should be compared in the way PCH and HCN have been contrasted herein in order to see exactly what should be done here.

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# Charge-Transfer Integral in Paramagnetic $\pi$ Molecular Crystals[1a]

**Zoltán G. Soos*[1b] and Paul J. Strebel**

*Contribution from the Department of Chemistry, Princeton University, Princeton, New Jersey 08540.* *Received October 26, 1970*

**Abstract:** An unambiguous separation of charge-transfer (CT) and electrostatic contributions is obtained in aromatic donor–acceptor crystals whose ground states contain stacks of ion radicals, since the activation energy for paramagnetism, $\Delta E_p$, arises from preferential CT stabilization of low-spin states. The magnitude of the Mulliken CT integral, $T$, is shown to be the geometric mean of $\Delta E_p$ and the lowest CT excitation. The values of $|T|$ in aromatic ionic crystals are in good agreement with theoretical estimates of $T$ and of CT stabilization in neutral $\pi$ molecular dimers.

Electrostatic and charge-transfer interactions both contribute[2] to the stability and geometry of complexes between electron donors, D, and acceptors, A, but their relative magnitudes are difficult to assess.[3] Theoretical treatments are necessarily approximate even for dimers, while experimental studies measure the sum of various contributions.

A clean separation of charge-transfer (CT) contributions is nevertheless possible in $\pi$ molecular crystals whose ground states contain stacks of ion radicals[4] of the type $\cdots D^+A^-D^+A^-\cdots$. CT interactions between adjacent radicals in a stack preferentially stabilize low-spin configurations and especially the diamagnetic ground state.[5] In the more commonly found *neutral* complexes of diamagnetic D and A molecules, the triplet state $D^+A^-$ involves an electron transfer. Magnetic excitations in ion-radical crystals,[4] on the other hand, require only low-energy spin flips and lead to a temperature dependence of the paramagnetism. Except for a small direct Heisenberg exchange,[4] the observed activation energy $\Delta E_p$ for $\chi T$, the paramagnetism times the absolute temperature, is solely due to CT contributions[5,6] and measures the thermal equilibrium density of unpaired spins above the diamagnetic ground state.

Electrostatic contributions, by contrast, reflect overall charge densities and are largely independent of spin orientations for small differential overlaps. All intermolecular separations exceed the van der Waals diameter in the $\pi$ molecular crystals discussed below except at most for the face-to-face separations between molecules in the same stack.[4,5] The differential overlaps are then negligible for molecules in different stacks and small even for adjacent molecules in the same stack.

The temperature dependence of the paramagnetism in ionic $\pi$ molecular crystals focuses attention on CT interactions and enables us to evaluate the magnitude of the Mulliken CT integral

$$T = \langle D^+A^-|\mathcal{H}|AD\rangle \qquad (1)$$

For largely *neutral* $a\pi$–$b\pi$ dimers in solution, the $|DA\rangle$ ground state contains small admixtures of the singlet excited state $|D^+A^-\rangle$. The *same* CT integral occurs in $\pi$ molecular crystals with *ionic* ground states and small admixtures of excited neutral contributions.[5,6] We have neglected the effects of the crystalline environment on the molecular orbitals, the usual molecular exciton approximation for small differential overlap. Similar values of $T$ are thus expected in neutral dimers and in ionic crystals when the geometries coincide.

In the following section, we show that the magnitude of $T$ is given by

$$|T| = [\Delta E_p \Delta E_{CT}(\ln 2/0.55x)]^{1/2} \qquad (2)$$

$\Delta E_p$ and $\Delta E_{CT}$ are the (measured) activation energies for paramagnetism and the lowest CT excitation, respectively. The dissimilarity parameter $x$ is defined by

$$x = 1 + \Delta E_{CT}/\Delta E_{CT}' \qquad (3)$$

and measures the dissimilarity of the radicals in the stack. In $\cdots D^+A^-D^+A^-\cdots$ stacks, $\Delta E_{CT}$ corresponds to the CT excitation $D^+A^- \rightarrow DA$, while $\Delta E_{CT}'$

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[2] J. L. Lippert, M. W. Hanna, and P. J. Trotter, *J. Amer. Chem. Soc.*, **91**, 4035 (1969); **90**, 285, 5358 (1968).

[3] (a) R. S. Mulliken and W. B. Person, *ibid.*, **91**, 3409 (1969); (b) see also "Molecular Complexes, A Lecture and Reprint Volume," Wiley, New York, N. Y., 1969, p 127; (c) M. J. S. Dewar and C. C. Thompson, Jr., *Tetrahedron Suppl.*, No. 7, 97 (1966).

[4] P. L. Nordio, Z. G. Soos, and H. M. McConnell, *Annu. Rev. Phys. Chem.*, **17**, 237 (1966); see also R. Foster and T. J. Thompson, *Trans. Faraday Soc.*, **59**, 296 (1963); Y. Matsunaga, *J. Chem. Phys.*, **41**, 1609 (1964); **42**, 1982 (1965); M. Ohmasa, M. Kinoshita, M. Sano, and H. Akamatu, *Bull. Chem. Soc. Jap.*, **41**, 1998 (1968).

[5] P. J. Strebel and Z. G. Soos, *J. Chem. Phys.*, **53**, 4077 (1970).

[6] H. M. McConnell, B. M. Hoffman, and R. M. Metzger, *Proc. Nat. Acad. Sci. U. S.*, **53**, 46 (1965).

represents the higher energy process, $D^{+}A^{-} \rightarrow D^{2+}A^{2-}$, in which a second electron is transferred. In free-radical crystals,[4] with stacks based a single radical, we have $\Delta E_{CT}' = \Delta E_{CT}$ and $x = 2$. $\Delta E_{CT}'$ is at least several times larger than $\Delta E_{CT}$ in ionic CT crystals, but has not been assigned in polarized absorption spectra.[7,8] Typical values of $x$ in such complexes thus range from 1.2 to 1.4, and the numerical coefficients in eq 2 are close to unity. In aromatic CT crystals with ionic ground states, we therefore find that $|T|$ *is simply the geometric mean of* $\Delta E_p$ *and* $\Delta E_{CT}$.

Observed $\Delta E_p$ and $\Delta E_{CT}$ values are shown in Table I for two 1:1 complexes of chloranil, with *p*-phenylenediamine (PD)[9,10] and with *N*,*N*,*N'*,*N'*-tetramethyl-*p*-phenylenediamine (TMPD),[8,11] as well as the 1:1 complex of TMPD with tetracyanoquinodimethane (TCNQ).[7,12] (The $\Delta E_{CT}$ value for PD–chloranil[10] is for a 5:3 complex, but is probably near that of the 1:1 complex; two distinct 1:1 TMPD–chloranil complexes are reported in ref 11 with slightly different $\Delta E_p$ values.) The values of $|T|$ in Table I are found from $(\Delta E_p \cdot \Delta E_{CT})^{1/2}$. Theoretical estimates for neutral a$\pi$–b$\pi$ dimers in which chloranil is the partner yield $T = -0.30$ eV, although that value "should not be taken as absolutely reliable"[3b] on account of severe quantum molecular approximations. It is nevertheless encouraging that such different approaches for largely neutral dimers and largely ionic crystals yield similar values for the magnitude of the Mulliken CT integral.

**Table I.** Mulliken CT Integral in Aromatic Ion-Radical Crystals[a]

| 1:1 crystal | Spin excitations $\Delta E_p$ | CT Band $\Delta E_{CT}$ | CT integral $\|T\| = (\Delta E_p \Delta E_{CT})^{1/2}$ |
|---|---|---|---|
| PD–chloranil | 0.13[b] | 1.17[c] | 0.39 |
| TMPD–chloranil | 0.13[d] (0.16)[d] | 1.1[e] | 0.38 (0.42) |
| TMPD–TCNQ | 0.07[f] | 0.95[g] | 0.26 |
| a$\pi$–b$\pi$ dimer (theoretical) | | | 0.30[h] |

[a] All quantities in electron volts. [b] See ref 9. [c] See ref 10. A 5:3 crystal was used. [d] See ref 11. Two different 1:1 complexes were found, with similar optical properties. [e] See ref 8. [f] See ref 12. A slightly larger value (0.075 eV) was reported by M. Kinoshita and H. Akamatu, *Nature* (*London*), **207**, 291 (1965). [g] See ref 7. [h] See ref 3b; for chloranil as acceptor in an a$\pi$–b$\pi$ complex.

## Magnitude of $T$

An average excitation energy for unpairing *all* the spins in a linear aromatic crystal is obtained from the theoretical treatment of CT stabilization in molecular stacks.[5] The large $\Delta E_p$ for the complexes in Table I indicates, however, that only a *few* spins are unpaired in thermal equilibrium at room temperature. A more refined derivation of $\Delta E_p$ is thus indicated, although it will be shown that the average excitation energy yields similar results for $|T|$.

As shown by Van Vleck[13] for free-radical crystals and by McConnell, *et al.*,[6] for paramagnetic CT complexes, an effective spin Hamiltonian

$$\mathcal{H}_{\text{eff}} = \sum_{n} J_{\text{eff}}[\vec{S}_n \cdot \vec{S}_{n+1} - (1/4)] \qquad (4)$$

describes the spin excitations for a stack of radicals when $|T| \ll \Delta E_{CT}$. The one dimensionality of the effective Hamiltonian is well established experimentally in systems with magnetically inequivalent stacks[9] and indicates the preferential $\pi$–$\pi$ interaction between molecules that are face to face in the same stack.[4,5] $\vec{S}_n$ in $\mathcal{H}_{\text{eff}}$ is a spin associated with the $n$th radical and $J_{\text{eff}}$ is antiferromagnetic (positive) when CT contributions dominate. We neglect in the following the direct Heisenberg exchange[4]

$$J_0 = \left\langle D^{+}(1)A^{-}(2)\left|\frac{e^2}{r_{12}}\right|D^{+}(2)A^{-}(1)\right\rangle \qquad (5)$$

for adjacent $D^{+}$ and $A^{-}$ radicals in comparison to the CT contribution. $J_0$ is at most of the order of 10 cm$^{-1}$ for electrons in $\pi$ systems separated by 3.5 Å, while the $\Delta E_p$ values in Table I are of the order of $10^3$ cm$^{-1}$.

We relate $J_{\text{eff}}$ and $|T|$ by observing that the exact[14] singlet ground state of $\mathcal{H}_{\text{eff}}$ for $J_{\text{eff}} > 0$ is

$$E_0^{\text{ex}}/N = -J_{\text{eff}} \ln 2 \qquad (6)$$

for a stack of $N$ radicals. The approximate self-consistent treatment of CT stabilization for the singlet ground state yields (from eq 3.23 and 5.14 of ref 5)

$$E_0^{\text{app}}/N = -T^2x/\Delta E_{CT} \qquad (7)$$

for small $|T|/\Delta E_{CT}$. The dissimilarity parameter $x$ is defined in eq 3 and is of the order of 1.2–1.4 for stacks of $D^{+}$ and $A^{-}$ radicals. Comparing eq 6 and 7, we obtain

$$J_{\text{eff}} = T^2x/\Delta E_{CT} \ln 2 \qquad (8)$$

and, as expected, $J_{\text{eff}} > 0$. Although eq 7 is a good approximation[5] even for moderate values of $|T|/\Delta E_{CT}$, it is then difficult to assess the validity of the effective spin Hamiltonian.

Finally, we relate $J_{\text{eff}}$ to the observed activation energy for paramagnetism, $\Delta E_p$, by solving $\mathcal{H}_{\text{eff}}$ self-consistently as a function of temperature.[15,16] The static susceptibility can be described by a single exponential for small, but not for large, densities of unpaired spins.[15] Since the complexes in Table I are unstable at high temperature, only small concentrations of unpaired spins are available in thermal equilibrium. For very low concentrations of unpaired spins, $\Delta E_p = 0.51J_{\text{eff}}$,[15] while the proportionality constant is about 0.6 for the higher spin densities in TMPD–TCNQ at room temperature.[12] The intermediate value of 0.55 for the proportionality constant is used to obtain eq 2 from eq 8.

The refined treatment for relating $\Delta E_p$ and $|T|$ involves several approximations, of which the hardest to assess is the use of $\mathcal{H}_{\text{eff}}$ for the $|T|/\Delta E_{CT}$ values in Table I. Fortunately, the cruder approximation of taking $\Delta E_p$ to be the average energy to unpair all spins leads

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(7) H. Kuroda, S. Hiroma, and H. Akamatu, *Bull. Chem. Soc., Jap.*, 41, 2855 (1968).

(8) B. G. Anex and E. B. Hill, Jr., *J. Amer. Chem. Soc.*, **88**, 3648 (1966).

(9) R. C. Hughes and Z. G. Soos, *J. Chem. Phys.*, **48**, 1066 (1968).

(10) V. A. Benderskii, I. B. Shevchenko, and L. A. Blyumenfeld, *Opt. Spectrosk.*, **16**, 467 (1964); *Opt. Spectrosc.* (*USSR*), **16**, 254 (1964).

(11) G. T. Pott and J. Kommandeur, *Mol. Phys.*, **13**, 373 (1967).

(12) B. M. Hoffman and R. C. Hughes, *J. Chem. Phys.*, **52**, 4011 (1970).

(13) J. H. Van Vleck in "Quantum Theory of Atoms, Molecules, and the Solid State," P.-O. Löwdin, Ed., Academic Press, New York, N. Y., 1966, p 475.

(14) L. Hulthén, *Ark. Mat. Astron. Fys.*, **26A**, 11 (1938).

(15) Z. G. Soos, *J. Chem. Phys.*, **43**, 1121 (1965).

(16) Z. G. Soos and R. C. Hughes, *ibid.*, **46**, 253 (1967).

to $\Delta E_p = E_0^{app}/N$ for moderate $|T|/\Delta E_{CT}$ values and, as seen from eq 7, simply reduces $|T|$ by $(\ln 2/0.55)^{1/2} = 1.12$. This error is comparable to the uncertainties in $\Delta E_p$ and $\Delta E_{CT}$. Since the dissimilarity parameter $x$ is of the order of 1.2–1.4, the numerical factors in eq 2 are indeed close to unity for aromatic CT crystals.

The magnitude of the Mulliken CT integral is thus accurately found in crystalline paramagnetic CT complexes from $(\Delta E_p \Delta E_{CT})^{1/2}$. No approximate quantum molecular calculations are required, although such methods may be used to obtain the sign of $T$. For smaller $\Delta E_p$ values than those in Table I, the direct Heisenberg exchange $J_0$ may not be negligible in comparison to the CT stabilization, and only an upper bound for $|T|$ is then given by $(\Delta E_p \Delta E_{CT})^{1/2}$.

## Discussion

While dimer geometries must be estimated, the crystal structures of many π molecular compounds are known.[4,17] The molecular planes in TMPD–chloranil are indeed perpendicular to the stack axis and permit optimal overlap.[17,18] The PD–chloranil planes are slightly tilted (~6°) on the basis of epr data,[9] while the TMPD–TCNQ planes are found crystallographically to be substantially tilted.[19] Increasing the donor and acceptor strengths thus need not favor maximum overlap in the crystal. It is fortunate that the *observed* crystal stacking is close to the *assumed* dimer geometry, although the different environments need not favor similar face-to-face geometries. In particular, the three-dimensional Madelung stabilization available in the crystal[5,20] leads to ionic ground states for the complexes in Table I, while aπ–bπ dimers in solution are largely neutral.

The sharp separation of π molecular crystals into largely neutral and largely ionic complexes[4] is also found theoretically[5,6] by considering the CT interactions in molecular stacks. The stabilization of both neutral and ionic lattices is given, to lowest order in $|T|/\Delta E_{CT}$, by eq 7 for each molecular overlap. The same stabilization of $T^2x/\Delta E_{CT} \sim 0.15$ eV for $x \sim 1.2$–$1.4$ is then expected for largely neutral aπ–bπ dimers (with $x = 1.0$) of comparable strengths whose geometries are close to the crystal geometry.

Hanna[2] has computed various electrostatic, charge-transfer, and exchange-repulsion contributions for the weaker neutral aπ–bπ complexes of tetracyanoethylene with benzene and with *p*-xylene. He estimates a CT stabilization of 2–3 kcal/mol. Our estimates for the CT stabilization in the stronger PD–chloranil and TMPD–chloranil complexes is about 0.15 eV (~3 kcal) and is an upper limit for aπ–bπ dimers unless significantly stronger π donors and acceptors are discovered. Our estimates for CT stabilization based on CT interactions in stacks of ion radicals thus support computations for neutral dimers and, indirectly, also support Hanna's suggestion that electrostatic contributions are the largest in π molecular systems.

In summary, the activation energy for paramagnetism, $\Delta E_p$, in ionic CT crystals arises from the preferential CT stabilization of low-spin states[5] and permits a direct evaluation of the Mulliken CT integral, $T$. Electrostatic contributions, by contrast, are independent of spin orientations in the limit of small differential overlaps. $\Delta E_p$ thus depends exclusively on the CT interactions, except for a small direct Heisenberg exchange contribution. The magnitude of $T$ was related to the geometric mean of $\Delta E_p$ and $\Delta E_{CT}$, the lowest CT excitation. Good agreement was found with theoretical estimates of $T$[3b] and of the CT stabilization[2] for neutral aπ–bπ dimers. The unusual magnetic properties of π molecular crystals with temperature-dependent concentrations of unpaired spins have been discussed elsewhere[4,9,12] and provide further information about the crystal states.

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(17) F. H. Herbstein, *Perspect. Struct. Chem.*, in press. This review summarizes crystallographic results and treats TMPD–chloranil as an ionic crystal.

(18) J. L. de Boer and A. Vos, *Acta Crystallogr., Sect. B*, **24**, 720 (1968).

(19) A. W. Hanson, *ibid.*, **19**, 610 (1965).

(20) J. I. Krugler, C. G. Montgomery, and H. M. McConnell, *J. Chem. Phys.*, **41**, 2421 (1964).