(14) Iodine-containing planes refer here to a family of planes which contain all or a large fraction of the iodine atoms in the structure and represent a predominant iodine-layering packing mode (i.e., these planes usually have an interplanar spacing of 3.4 Å or greater).

(15) The high stereospecificity of this kind of reactant lattice control in centrosymmetric crystals of I-α suggests the possibility that a chiral reactant lattice could preferentially orient one enantiomeric product lattice. If a chemically racemic product were formed during a single-crystal reaction, the chiral reactant lattice might be able to effect a chemical resolution of the racemate by inducing crystallization of only one enantiomeric crystal form. Likewise, a crystallographic resolution of nonchiral product molecules which pack in enantiomeric space groups is also theoretically possible in a topotactic reaction.

(16) E. Shefter and W. Wolf, *Nature* (*London*), **203**, 512 (1964).

(17) This would represent a Lonsdale twin phase generated by conservative twinning about the product lattice point-group symmetry elements.

(18) Attempts to effect this conversion by diazomethane esterification of single crystals of II were unsuccessful.[6]

(19) In the conversion of anthracene photooxide to anthraquinone, one of the first examples of an organic topotactic reaction, Lonsdale clearly demonstrated the importance of aligning molecular stacks of reactant and product molecules.[20] In this case the molecular stacks were defined by close-packed aromatic rings, since there were no heavy-atom substituents.

(20) K. Lonsdale, E. Nave, and J. F. Stephens, *Philos. Trans., R. Soc. London, Ser. A*, **261**, 1 (1966).

(21) Precisely the same topotactic relationships exist between twin phases of II formed from 3-oxo-3*H*-2,1-benzoxiodol-1-yl-*o*-fluorobenzoate, but in this case the $(100)_{\text{II}}$ twin plane is parallel to the mirror plane of the reactant.[11] The twin phases are, thus, conservative twins resulting from twinning about the point-group symmetry elements of reactant. The twin phases formed from I-β, however, are not conservatively twinned, but still occur in equal concentrations, giving credence to the postulate made by Gougoutas that the specific topotaxy between reactant and twinned product phases may be established in order to produce a favorable interphase relationship between the product twins.[11]

(22) The vector relationships were derived from fundamental crystallographic properties of the direct and reciprocal basis sets, as defined by Buerger.[23]

(23) M. J. Buerger, "Crystal Structure Analyses", Wiley, New York, N.Y. 1960, p 407.

(24) The interplanar spacings are the same when both $\{h_i\}$ and $\{k_i\}$ are prime numbers; when one set is not prime the interplanar spacings are integer multiples of each other.

Molecular Criteria of Solid-State Structure in Organic Charge-Transfer Salts. 2. Effect of Methyl Substitution on Stacking Interactions of *p*-Phenylenediamine Cation Radicals

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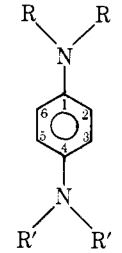
Abstract: The ability of *p*-phenylenediamine cation radicals to self-associate and form sandwich dimers or higher aggregates was found to be a function of methyl substitution, TMPD$\cdot^+$ (*N,N,N′,N′*-tetramethyl-*p*-phenylenediamine) < DMPD$\cdot^+$ (*N,N*-dimethyl-*p*-phenylenediamine) ≈ PPD$\cdot^+$ (*p*-phenylenediamine). The gas-phase ionization potentials or electrochemical disproportionation ($2D^+ \rightleftarrows D^0 + D^{2+}$) energies showed no correlation with the observed association properties. However, the enthalpy of dimerization (ΔH) was found to be proportional to the experimental unpaired π-electron spin density at the terminal ring carbons of the ion radicals. Steric considerations were shown to be relatively unimportant in the self-association processes. The relationship between these molecular data and the solid-state structure of salts formed by these cation radicals was discussed.

Since the initial discovery that certain organic ion radicals form stable solids,[1] a wide variety of these solids, displaying a surprising range of physical properties, has been synthesized and studied.[2] In the last 15 years, growing interest based on the pioneering research of the duPont group[3] has centered on the preparation of increasingly more metallic organic charge-transfer salts. Until recently, however, synthetic efforts to prepare molecules which formed solids with specific types of physical properties have been largely guided by trial and error or structural analogy to known molecules. Fortunately, concerted attempts are currently being made to understand and control the relationship[4-6] between molecular structure and solid-state properties for these materials in hopes of making the selection of potentially interesting molecules less haphazard.

In a general sense the connection between the molecular structure of the constituent molecules D (Donor) and A (Acceptor) and the physical properties of the resulting solid is related to the way in which the D$\cdot^+$ and A$\cdot^-$ ion radicals stack in the solid state.[2,4] Since the most interesting solid-state effects appear to be associated with the formation of separate, equally spaced infinite stacks of planar D$\cdot^+$ or A$\cdot^-$ species,[7] it is important to understand how changes in molecular architecture affect this type of ion-radical stacking.

To begin to answer this question we have studied the physical properties of a series of donor ion radicals which form self-stacked bromide salts, D$\cdot^+$Br$^-$. The presence of only one type of organic ion radical (i.e., donor) should minimize the presence of complicating interstack interactions. The ion-radical donors studied are a homologous series of aromatic diamines:[8] *N,N,N′,N′*-tetramethyl-*p*-phenylenediamine (TMPD),



TMPD, R = R′ = CH_3
DMPD, R = H; R′ = CH_3
PPD, R = R′ = H

N,N-dimethyl-*p*-phenylenediamine (DMPD), and *p*-phenylenediamine (PPD). We seek to understand why removal of two methyl groups from one side of the molecule in going from TMPD to DMPD results in a corresponding decrease in

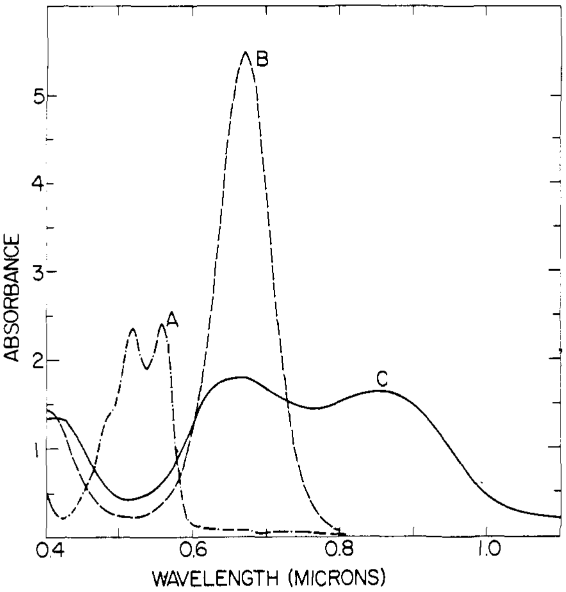


Figure 1. Effect of aggregation on the electronic spectrum of DMPD$\cdot^+$ cation radical; DMPD$\cdot^+$Br$^-$ (5.55×10^{-4} M) in ethanol-ether (2:1) solution. (A) Monomer spectrum at 298 K; (B) Dimer spectrum obtained when solution rapidly cooled to 130 K; (C) Aggregate spectrum when B warmed to 200 K. See text for details.

the intrastack distance of ~0.4 Å[9,10] for the corresponding isomorphous bromide salts.

Specifically, we show how molecular parameters for the isolated ion radicals and the dimers of these radicals can be used to analyze the effect of methyl substitution in these systems. While the steric and electronic influence of aliphatic substituents on molecular reactivity has been well documented,[11] very little is known about the effects of systematically changing the molecular substituents on the stacking of ion radicals in charge-transfer salts. Invariably, the rather dramatic changes observed in going to the substituted species[12] have either not been discussed[12a] or have been tentatively explained by steric hindrance.[12b]

Experimental Section

Materials. *N,N,N',N'*-Tetramethyl-*p*-phenylenediamine (Aldrich) and *p*-phenylenediamine (Aldrich) were purified by repeated vacuum sublimation. *N,N*-Dimethyl-*p*-phenylenediamine (Eastman) was purified by initial vacuum distillation followed by a final sublimation step. The bromide salts of the donor cation radicals were prepared by the method of Michaelis and Granick.[13] All compounds were stored under an inert atmosphere until use. Tetraethylammonium perchlorate, polarographic grade (South Western Analytical Chemicals) was dried under vacuum at 60 °C for several days. Acetonitrile for cyclic voltammetry was purified by an abbreviated method of O'Donnell and Ayers.[14] All solvents were saturated with nitrogen prior to electrochemical or optical measurements (Cary 14 spectrophotometer).

Procedure. Cyclic voltammograms were run in acetonitrile solvent at a platinum working electrode with a sweep rate of 0.20 V/s (volts vs. SCE). The solutions contained 5×10^{-5} M of the neutral donor molecules and 0.1 M tetraethylammonium perchlorate.

The experimental hyperfine splitting constants of the cation radicals TMPD$\cdot^+$,[15a] DMPD$\cdot^+$,[16] and PPD$\cdot^+$ [15b] were used to calculate the relevant π spin densities by employing the theoretically optimized Q type parameters of Smejtek et al.[17]

Results

Selected electronic properties relating to the electron-donor ability of the three *p*-phenylenediamine compounds are given in Table I. In the series, the tetramethyl-substituted derivative I is easiest to ionize, as seen from its very low values for peak oxidation potential (ϵ_1) and ionization potential (I_p). In fact, TMPD has one of the lowest I_p values recorded for any benzenoid hydrocarbon.[18] Stepwise removal of the methyl groups leads to expected increases in ϵ_1, I_p, and the electron affinity (E_a) of D$\cdot^+$. The values of the second oxidation potentials (ϵ_2) are found to increase in parallel with the first oxidation potentials, leading to a relatively constant value for their difference, Δ. Apparently, substitutional changes in these systems do not affect the value of this disproportionation parameter.

Table I. Electronic Properties of Aromatic *p*-Phenylenediamine Donor Molecules[a]

Compd	$\epsilon_1{}^b$	$\epsilon_2{}^b$	$\Delta\epsilon^c$	$I_p{}^d$	$E_a{}^e$
TMPD	0.13	0.72	0.59	6.33	5.65
DMPD	0.25	0.83	0.58	6.84	5.95
PPD	0.30	0.86	0.56	7.26	6.21

[a] Energy in eV. [b] Value of peak potentials from cyclic voltammetry for D $\rightarrow$ D$\cdot^+$ (ϵ_1); D$\cdot^+$ $\rightarrow$ D^{2+} (ϵ_2). [c] $\Delta\epsilon \doteq \epsilon_2 - \epsilon_1$. [d] Electron impact ionization potential vapor phase. Unpublished results of C. E. Klots and R. N. Compton. Cf. ref 19b for experimental details. [e] E_a = electron affinity of D$\cdot^+$; cf. T. Sakata, T. Okai, H. Sugimato, and H. Tsubomura, *Bull. Chem. Soc. Jpn.*, **46**, 2698 (1973).

It has recently been suggested that small values of Δ and I_p may indicate likely molecular candidates for organic metals.[4] In the homologous series considered here, however, the simple trend to higher ionization potentials does not correlate with changes in intermolecular or solid-state properties (see below). Another good organic donor, tetrathiafulvalene, with its higher I_p (6.9 eV)[19] and lower Δ (0.37 eV),[20] forms a conducting solid with TCNQ[21a] and halogens,[22,23] whose x-ray structure and properties are in marked contrast to the corresponding TMPD[9,21b] solids. Since these simple parameters undoubtedly reflect more complex differences between these species, we were led to consider more basic parameters of ion radicals[24] that would be potentially more sensitive to changes in their steric and electronic properties as a function of substitution. Specifically, we felt that the known ability of planar organic cation[25] and anion radicals[26] to form dimers could be used as a probe of the intrastack interactions of the type experienced by the ion radicals in the solid state.

In Figure 1 is shown the visible near ir spectrum of DMPD$\cdot^+$Br$^-$ (5.55×10^{-4} M) dissolved in ethanol-ether (2:1) solution. At 298 K the spectrum (A) is that of the monomeric cation radical. Rapid cooling of the solution to 130 K (B) yields the dimeric cation radical, as identified by its characteristic absorptions.[27,28] When this matrix is allowed to soften by warming up to 200 K, a new transition is seen in the spectrum (C) at 860 nm. Spectrum C is also obtained by slow cooling (1-2 h) to 200 K from room temperature. The monomer spectrum reappears on warming to 298 K, and continued temperature cycling yields these same spectra. At *lower* concentrations only the previously studied monomer-dimer equilibrium is observed.[29]

The new spectrum which results from warming a viscous glass containing a relatively high concentration of DMPD$\cdot^+$ dimers bears a striking resemblance to the absorption spectrum of crystalline DMPD$\cdot^+$Br$^-$.[9,30] As a result, it is tempting to tentatively describe the process which is occurring as formation of solid-state aggregates via dimeric precursors. The association of dye molecules to form higher aggregates[31a] has been known for some time and, under very analogous conditions of matrix softening, anthracene has been shown to form stable higher aggregates.[31b] In addition, a number of authors have commented on the apparent cooperativity of aggregate formation once sufficient incipient dimerization has occurred.[32]

Under identical experimental conditions PD$\cdot^+$Br shows similar behavior. However, with TMPD$\cdot^+$Br$\cdot^-$ there was no

Table II. Properties of *p*-Phenylenediamine Cation Radical Dimers[a]

Dimer	λ_{CT},[b] nm	$\Delta\nu$,[c] cm^{-1}	f_{CT}[d]	ΔH,[e] kcal/mol
$(TMPD^+)_2$	765	6650	0.16	−5.6
$(DMPD^+)_2$	665	9770	0.66	−8.0
$(PPD^+)_2$	605	9440	0.68	−8.2

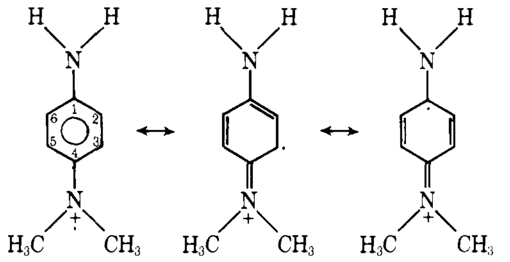
[a] Spectral data in ETOH–ether (2:1). [b] λ_{CT} is position of lowest energy charge-transfer dimer absorption. [c] Frequency difference between first two optical transitions: $\Delta\nu = (\nu_D - \nu_{CT})$. [d] Calculated oscillator strength; cf. ref 28. [e] Measured enthalpy of dimerization; cf. ref 28.

evidence of aggregate formation. The characterization data for the three ion-radical dimers (Table II) indicate that removal of two methyl groups from TMPD leads to increases in the enthalpy of dimerization (ΔH) and the optical splitting ($\Delta\nu$) and oscillator strength (f) of the intradimer charge-transfer (CT) transition.[25] Subsequent removal of the other two methyl groups to give PPD has a negligible effect on these parameters. The increases in the value of ΔH with loss of methyl substituents are reasonably well tracked by parallel changes in the $\Delta\nu$ parameter. Unfortunately, it is difficult to say at this time how this increased "interaction" leads to differences in the formation of aggregates without more knowledge of the detailed mechanism of crystallization (especially cooperative effects) in these systems. However, in the absence of substantial changes in entropic interactions for these species,[33] ΔH values for trimers, tetramers, etc. that mirror the dimerization results could lead to the large differences in relative equilibrium constants for solid-state aggregates that we have apparently observed.

In order to understand the reasons for the increased optical and thermodynamic interactions in the dimers of ion radicals II and III, the π-electron spin densities for each of these species were calculated (cf. Table III). Inasmuch as the dimerization processes of these ion radicals in solution[34,35] and in the solid state[25a] involve paramagnetic monomer–diamagnetic dimer equilibria, it was felt that specific changes in the unpaired spin-density distribution as a function of substitution could influence the spin-pairing process.

The changes in total spin density for these molecules (Table IV) indicate that stepwise loss of methyl groups tend to push spin density off of the external nitrogens and into the ring, where it is taken up by the para substituent bearing carbons 1 and 4. In going from TMPD·$^+$ to PPD·$^+$, the total increase in spin density at these positions of almost 50% implies that quinoidal resonance forms II and III (shown for DMPD) have become more important.

The predictive ability of valence-bond structures in these systems has been previously shown.[36] For the asymmetrically substituted DMPD·$^+$ cation, consideration of the two possible structures III suggests greater spin density at the terminal C(1) vs. C(4) position due to the heightened ability of the methyl substituents to stabilize positive charge, A quantitative estimate of the stabilization was determined from the spin density inequivalence at the 2,6 vs. the 3,5 positions (Table III). It is seen that 65% of the total spin on these meta carbons resides at C(3), C(5). This weighting factor was used to evaluate $\rho_{C(1)}{}^{\pi}$ and $\rho_{C(4)}{}^{\pi}$ from the total spin density (0.201) at these positions.



I

II (four forms)

III (two forms)

Discussion

Steric vs. Electronic Effects in the Dimerization of *p*-Phenylenediamine Cation Radicals. The differences in the electronic interactions and thermodynamic stability of the dimers of these cation radicals were recently ascribed to the increased steric repulsion between the methyl groups in two neighboring TMPD·$^+$ radicals and the absence of these steric effects for DMPD·$^+$ and PPD·$^+$ dimers.[28] Steric effects have also been implicated in the dimerization of neutral free radicals[37,38] and porphyrin cation radicals.[25c] On the other hand, the potential importance of electronic effects influencing dimerization reactions have also been considered,[25c,38] but the available experimental data have not allowed for unambiguous assessment of the relative importance of this factor.

We were motivated by the belief that, in the absence of other factors, the thermodynamics of dimerization in a homologous series of cation radicals, could be dependent on the unpaired spin density at the sites of maximal *inter*molecular interaction. Recently it has been recognized that the spin-density distribution in a molecule can play an important part in determining chemical reactivity. In the photochemical reactions of β,γ-unsaturated ketones,[39] the charge-transfer complex formation of indoles with benzenoid acceptors,[40a] or halogenated alkanes with nitroxide radical,[40b] and in predicting the orientation of aromatic substitution reactions,[41] it has been shown that the course of the chemical reaction can be rationalized by considering the spin-density distribution at specific sites in the molecule. While most workers studying molecular reactivity have not considered the functional dependence on spin density, Epiotis[41] has suggested that the stabilization energy attending the interaction of two molecules is proportional to $(\rho_i\rho_j)\cdot\gamma_{ij}{}^2/\Delta E$, where ρ_i and ρ_j is the spin density of the *i*th and *j*th atomic orbital of each molecule, γ_{ij} is the resonance integral between the interacting orbitals, and ΔE is the energy difference between the appropriate orbitals of the reacting aromatic–nucleophile pair. In the absence of different electronic

Table III. Spin-Density Distributions[a] in *p*-Phenylenediamine Radical Cations[b]

Cation	$\rho_{C(1,4)}{}^{\pi}$	$\rho_{C(2,6,3,5)}{}^{\pi}$	$\rho_N{}^{\pi}$	q_N[c]
TMPD·$^+$	0.089	0.071	0.268	0.492
DMPD·$^+$	0.130[d] (1)	0.051 (2,6)	0.194 (1)	0.409 (1)
	0.071[d] (4)	0.095 (3,5)	0.307 (4)	0.536 (4)
PPD·$^+$	0.131	0.086	0.217	0.435

[a] Calculated from $\rho_i = a_iQ_i$; a_i values from ref 15 and 16. Q_i values used were $|Q_{CH}{}^{H}| = 27.8$, $|Q_{NH}{}^{H}| = 26.61$, $|Q_{NCN_3}{}^{H}| = 25.22$ G (cf. ref 17). [b] Numbers in parentheses refer to atomic positions in molecule. [c] q_N is positive charge density at nitrogen; $q_N = 1.122\rho_N{}^{\pi} + 0.192$ (cf. ref 16). [d] See text for discussion.

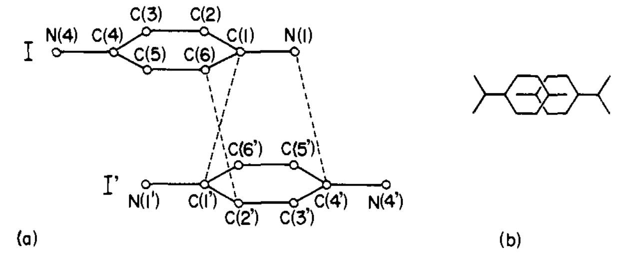


Figure 2. Intermolecular stacking in TMPD·$^+$Br$^-$ and DMPD·$^+$Br$^-$ (methyl substituents not shown). (a) Stacking along the *c* axis; dotted lines identify shortest interatomic contacts; (b) Intermolecular overlap looking down *c* axis. For DMPD, CH_3 groups at N(4) and N(4′).

Table IV. Total Unpaired Spin Densities

Cation	$\Sigma_{1,4}\rho_{C_i}{}^{\pi}$	$\Sigma_{2,3,5,6}\rho_{C_i}{}^{\pi}$	$\Sigma_{1,4}\rho_{N_i}{}^{\pi}$
TMPD·$^+$	0.178	0.284	0.536
DMPD·$^+$	0.201	0.292	0.501
PPD·$^+$	0.262	0.304	0.434

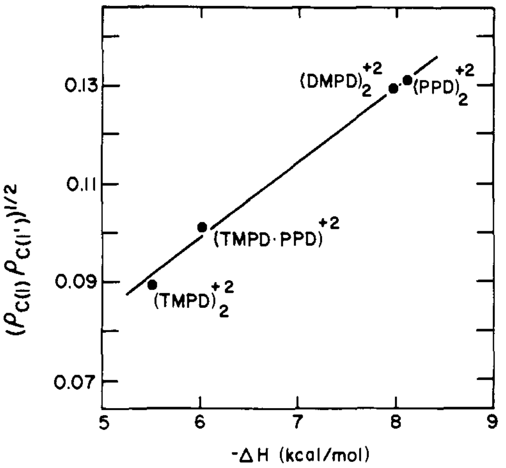


Figure 3. Enthalpy of dimerization (ΔH) for TMPD, DMPD, PPD, and mixed TMPD–PPD dimers vs. $(\rho_i\rho_j)^{1/2}$ for interaction at C(1),C(1′) sites.

contributions to bonding for different positions in the molecules, γ_{ij} would reflect the influence of steric interactions on stabilization energy.[43]

In a simple one-electron treatment based on the interaction of the unpaired electron in the HOMO (frontier orbital[42]) of a cation radical, the stabilization energy for formation of a dimer was found[43] to be $(\rho_i\rho_j)^{1/2}\beta_{ij}$, with ρ_i and ρ_j the spin density at sites *i* and *j* and β_{ij} the respective resonance integral. In order to evaluate the electronic interactions in dimer formation we assume that the relative orientation of the two cation radicals is the R-EB (ring-external bond) sandwich overlap structure (Figure 2). This type of overlap is very commonly encountered for stacking of planar organic ion radicals[2,7,19] and is the way in which the *p*-phenylenediamine cation radicals are known to stack in the solid state as bromide salts.[9,10] Additional support for this structural assumption comes from the large similarity in optical spectra[9,30,44] for TMPD·$^+$ dimers (solution) and TMPD·$^+$Br$^-$ in the solid state.[9]

The pairs of atoms of closest approach in this dimer configuration are: N(1),C(4′); C(1),C(1′); and C(6),C(2′).[10] In order to test the electronic interaction mechanism introduced above, the spin-density product function $(\rho_i\rho_j)^{1/2}$ for interaction at the C(1)···C(1′) sites was plotted with respect to the experimental ΔH values for dimerization (Figure 3). The data for the three dimers previously discussed are included, as well as data for the asymmetric dimer formed from the TMPD and PPD free radicals.[27a] It is seen that the spin density of functions at the terminal carbon positions C(1),C(1′) increases in going from the TMPD to the PPD dimer, paralleling the rise in the $-\Delta H$ value. Perhaps fortuitously (see below), the correlation was found to be linear within the experimental error in the determination of ΔH.

Quantitative evaluation of the *total* orbital overlap contribution to the dimer stabilization energy due to interactions at the other atomic sites of closest approach and the other possible molecular orientations (i.e., for DMPD) is not possible here. This would require evaluating how the resonance integrals β_{ij} depend on atomic position. Qualitatively, however, we have found that these additional factors lead to results which are quite similar to those of Figure 3. Consideration of several trial total spin-density product functions[43] indicate that the true increase in going from the TMPD to the PPD dimer is probably less than that shown for just the C(1),C(1′) interaction.

A more serious indictment of Figure 3 concerns the limitations of ΔH as a true reactivity index. Undoubtedly, the measured ΔH values contain spin-independent contributions due to solution and polarization effects[25c] and from classical dispersion and van der Waals' forces. The latter effects have been extensively implicated as the driving force for dimerization of *closed-shell* ionic dye molecules.[31,32] More extensive investigations on the thermodynamic effects of solvent, ionic strength, and counterions for the dimerization of ion radicals will be needed to unravel the importance of these other factors.

In the homologous series considered here these factors may not change drastically in going from one cation radical to another. Under these conditions, it is clear that there is a qualitative correlation between the changes in the spin density of the ion radicals and the thermodynamics of dimerization. Consequently, steric effects do not appear to be of major importance in the "self-stacking" dimerization reactions of these species. This conclusion is corroborated by examination of CPK (Corey–Pauling–Kolton) space-filling molecular models.[45]

Relationship between Molecular Parameters and Solid-State Structure. It was shown above that TMPD cation radical differs significantly from DMPD and PPD in its aggregation behavior and in the interaction strength of the dimeric species formed in fluid media. Changes in the cation spin-density distribution with molecular substitution were used to explain the observed differences. However, the relationship between molecular or dimeric properties of cation radicals may not reflect the stacking interactions present in the solid state. Therefore, an important question to ask at this point is how well do the parameters considered here relate to the solid-state structure of *p*-phenylenediamine salts?

In the solid state as bromide salts, the TMPD·$^+$ or DMPD·$^+$ cation radicals stack in an identical (ring-external bond, cf. Figure 2b) manner. However, the unit-cell[46] dimensions for the TMPD·$^+$ salt are increased; hence the intermolecular overlap distances are significantly enlarged. The interplanar distance in TMPD·$^+$Br$^-$ of 3.52 Å is significantly reduced to 3.11 Å in the DMPD·$^+$ derivative, with the shortest atomic contacts in these systems being 3.63 and 3.21 Å, respectively.[9,10] If there were a relationship between the strength of bonding in the dimers and the solid state, then the similarities observed for the PPD and DMPD cation spin densities and their dimers should lead to similar solid-state structures. The x-ray structure of PPD·$^+$Br$^-$ has not been determined. However, the results of optical,[9] magnetic,[47] and infrared measurements[48] all support the contention that both DMPD$^+$Br$^-$ and PPD$^+$Br$^-$ crystallize in similar, strongly overlapped stacking patterns in the solid state.

Table V. Crystallographic Data for Salts of *p*-Phenylenediamine Cation Radical

		Interatomic distance,[b] Å			
Compd	Stacking,[a] *d*(Å)	C(2)–C(3)	C(1)–C(2)	C(1)–N(1)	Ref
$TMPD^{\cdot+}(TCNQ)_2^{\cdot-}$	S-EB, 3.51	1.367 (4)	1.418 (4)	1.373 (4)	*g*
(TMPD)(TCNQ)	R-EB, 3.27[c]	1.374 (10)	1.416 (7)	1.365 (7)	*h*
$TMPD^{\cdot+}ClO_4^{\cdot-}$ (RT)	EB, 3.55	1.365 (6)	1.426 (3)	1.359 (5)	*i*
$TMPD^{\cdot+}ClO_4^{\cdot-}$ (LT)[d]	EB, 3.10[e]	1.365 (2)	1.431 (2)	1.346 (2)	*j*
$DMPD^{\cdot+}Br^-$	R-EB′, 3.10	1.313 (20)	1.430[f]	1.270[f]	*k*

[a] Stacking configuration types with interplanar distances (*d*) are EB, external bond; S-EB, shifted external bond; R-EB, ring-external bond (*C*2/*m* space group); R-EB′, ring-external bond (*Cmcm* space group). All stacking is segregated with individual chains of radicals except where indicated. [b] Interatomic distance in ångstroms with standard deviations given in parentheses. [c] Alternating stack structure; i.e. $D^+A^-D^+A^-$ linear chain. [d] Structure measured at 110 K. Compound undergoes reversible phase transition at 186 K. [e] Interplanar distance between dimers; shortest intermolecular distance is 3.31 Å (N(1)–C(2)). [f] Average value of bond lengths used, see text. [g] A. W. Hanson, *Acta Crystallogr., Sect. B*, **24,** 768 (1968). [h] A. W. Hanson, *Acta Crystallogr.*, **19,** 610 (1965). [i] J. L. de Boer and A. Vos, *Acta Crystallogr., Sect. B*, **28,** 835 (1972). [j] *Ibid.*, **28,** 839 (1972). [k] Cf. ref 10.

The connection between dimeric interaction and "bonding" in the solid state is further seen from the changes in bond lengths of these cation radicals as a function of intermolecular stacking distance and solid-state aggregation (Table V). In going down the table it can be seen that the C(1)–C(2) distances get longer while C(1)–N(1) distances get shorter. For the three self-stacked $TMPD^{\cdot+}$ salts the bond length changes parallel the change in aggregation in these systems[2,8] from isolated cation monomer ($TMPD^{\cdot+}(TCNQ)_2^{\cdot-}$) to weakly interacting monomer ($TMPD^{\cdot+}ClO_4^-$ (RT) to ion-radical dimer ($TMPD^{\cdot+}ClO_4^-$ (LT)). The decrease in the intermolecular stacking distance (3.606–3.313 Å),[49] the change in spin from doublet to singlet,[2] and the alternations in the interatomic distance (Table V) which accompany the solid-state dimerization of $TMPD^{\cdot+}ClO_4^-$ imply the formation of new bonds (albeit weak ones) between the ion radicals in this process. The observed changes in interatomic distances with increasing interstack interactions suggest a trend towards quinoidal resonance forms II and III, which have increased unpaired spin density available for bonding on the terminal ring carbons. Furthermore, the unique thermal ellipsoids of C(1) in the crystal structure of $DMPD^{\cdot+}Br^-$,[10] the compound with the largest solid-state interactions, are consistent with bonding at this position.

We have suggested that the ΔH of dimerization of the *p*-phenylenediamine cation radicals measured in solution may provide a criterion for estimating the strength of the inter-radical bonding in the solid state. More extensive electronic interaction between the cation radicals in a dimer leads to a larger negative value of dimerization, which correlates with the shorter interradical bond distances observed for the systems considered here. Undoubtedly, the situation is more complex and the relative contributions to the bonding by other, more subtle, factors must be considered. For instance, changing the anion is known to alter the details of intermolecular overlap for these cations, yet the Br^- cation distances may be large enough here to preclude this factor from being significant. In addition, the possible long-range (termolecular or greater) effects of stacking between organic ion radicals leading to stabilization of specific crystal structures is not understood at present. However, the x-ray data for compounds of the $TCNQ^{\cdot-}$ anion[2,7,18] show that long-range order in these systems is not a necessary prerequisite for particular overlap patterns or short intermolecular spacings. Finally, the mechanism of Coulombic stabilization of these highly charged aggregates, both in solution and in the solid state, needs to be further explored.

DA vs. Self Stacking for *p*-Phenylenediamine Cation Radicals in the Solid State. The cation radicals discussed here form "self" stacked structures in the solid state for inorganic cations such as Br^- or ClO_4^-. With common organic anions like $TCNQ^-$ or *p*-chloranil⁻, however, the x-ray[18] and physical characterization[2,50] data indicate that only alternating (DA) structures are formed. The reasons for this difference are not well understood. In contrast to this situation is that of the tetrathiafulvalene (TTF) donor molecule. It is electronically similar to TMPD,[24] but does not share with it the unique benzenoid character discussed above. TTF and most of its derivatives do not show strong tendencies to form DA stacked salts with TCNQ.[5,6,12] On the contrary, TTF forms highly conducting self-stacked solids with TCNQ[21a] and halogens.[22,23] In marked contrast to the 1:1 donor halides discussed here, $TTF^{\cdot+}$ crystallizes as a mixed-valent[23] halide salt ($TTFX_{0.8}$) which contains molecules of formally neutral TTF. This "partial charge-transfer" along the TTF stack also appears to be important with an organic anion like $TCNQ^-$, since photoemission,[51] optical,[52] and x-ray[53] data indicate less than full charge transfer in (TTF)(TCNQ). This comparison between TTF and TMPD suggests that the inability of $TMPD^+$ to form a (TTF)(TCNQ)-like structure could be due to the inability of this donor to form a mixed-valence stack. To test this intriguing hypothesis, experiments to elucidate the molecular parameters necessary for formation of mixed-valence halide salts are currently underway.

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References and Notes

(1) R. Willstätter and J. Piccard, *Ber.*, **41**, 1945 (1908).
(2) For a recent review see Z. G. Soos, *Annu. Rev. Phys. Chem.*, **25**, 121 (1974).
(3) L. R. Melby, R. J. Harder, W. R. Hertler, W. Mahler, R. E. Benson, and W. E. Mochel, *J. Am. Chem. Soc.*, **84**, 3374 (1962).
(4) A. F. Garito and A. J. Heeger, *Acc. Chem. Res.*, **7**, 232 (1974).
(5) A. N. Bloch, D. O. Cowan, and T. O. Poehler in "Energy and Charge Transfer in Organic Semiconductors", K. Masuda and M. Silver, Ed., Plenum Press, New York, N.Y., 1974.
(6) E. M. Engler and V. V. Patel, *J. Am. Chem. Soc.*, **96**, 7376 (1974).
(7) Cf. R. P. Shibaeva and L. O. Atovmyan, *J. Struct. Chem.*, **13**, 546 (1972) for a brief review of the most commonly encountered types of molecular stacking in these compounds.
(8) These substituted aromatic diamines are reviewed in: (a) A. R. Forrester, J. M. Hay, and R. H. Thomson, "Organic Chemistry of Free Radicals",

Academic Press, New York, N.Y., 1968; (b) S. F. Nelson in "Free Radicals", Vol. II, J. K. Kochi, Ed., Wiley Interscience, New York, N.Y., 1973.

(9) J. Tanaka and M. Mizuno, *Bull. Chem. Soc. Jpn.*, **42**, 1841 (1969).

(10) J. Tanaka and N. Sakabe, *Acta. Crystallogr., Sect. B*, **24**, 1345 (1968).

(11) J. Hine, "Physical Organic Chemistry", 2d ed, McGraw-Hill, New York, N.Y., 1962.

(12) For substitutional changes in donor TCNQ (cf. ref 3) compounds, the following effects were observed; (a) tetramethyl substitution on tetraselenofulvalene (cf. ref 6); nonconducting phase isolated: K. Bechgaard, D. O. Cowan, and A. N. Bloc, *J. Chem. Soc. Chem. Commun.*, 937 (1974); (b) tetrapropyl substitution on tetrathiofulvalene; conductivity decreased by six orders of magnitude: L. B. Coleman, F. G. Yamagishi, A. F. Garito, A. J. Heeger, D. J. Dahm, M. G. Miles, and J. D. Wilson, *Phys. Lett.*, in press; (c) ethyl substitution on *N*-methylphenazine; conductivity decrease of 11 orders of magnitude: L. R. Melby, *Can. J. Chem.*, **43**, 1448 (1965).

(13) L. Michaelis and S. Granick, *J. Am. Chem. Soc.*, **65**, 1747 (1943).

(14) J. F. O'Donnell, S. T. Ayers, and C. K. Mann, *Anal. Chem.*, **37**, 1161 (1965); J. A. Lanning and J. Q. Chambers, *ibid.*, **45**, 1010 (1973).

(15) (a) J. R. Bolton, A. Carrington, and J. dos Santos-Veiga, *Mol. Phys.*, **5**, 615 (1962); K. H. Hausser, *ibid.*, **7**, 194 (1964); (b) L. H. Piette, P. Ludwig, and R. N. Adams, *Anal. Chem.*, **34**, 916 (1962); M. T. Melchior and A. H. Maki, *J. Chem. Phys.*, **34**, 471 (1961).

(16) B. M. Latta and R. W. Taft, *J. Am. Chem. Soc.*, **89**, 5172 (1967).

(17) P. Smejtek, J. Honzl, and V. Metalová, *Collect. Czech. Chem. Commun.*, **30**, 3875 (1965).

(18) F. H. Herbstein in "Perspectives in Structural Chemistry", Vol. IV, J. D. Dunitz and J. A. Ibers, Ed., Wiley, New York, N.Y., 1971.

(19) (a) R. Gleiter, E. Schmidt, D. O. Cowan, and J. P. Ferraris, *J. Electron Spectrosc. Relat. Phenom.*, **2**, 207 (1973); (b) C. E. Klots, R. N. Compton, and V. F. Raaen, *J. Chem. Phys.*, **60**, 1177 (1974).

(20) D. L. Coffen, J. Q. Chambers, D. R. Williams, P. E. Garrett, and N. D. Canfield, *J. Am. Chem. Soc.*, **93**, 2258 (1971); E. M. Engler, F. B. Kaufman, D. C. Green, C. E. Klots, and R. N. Compton, *ibid.*, **97**, 2921 (1975).

(21) (a) For (TTF)(TCNQ) cf. J. Ferraris, D. O. Cowan, V. Walatka, and J. H. Perlstein, *J. Am. Chem. Soc.*, **95**, 948 (1973); (b) For (TMPD)(TCNQ) cf. ref 2.

(22) (a) F. Wudl, D. Wobschall, and E. J. Hufnagel, *J. Am. Chem. Soc.*, **94**, 670 (1972); (b) F. B. Kaufman, E. M. Engler, D. C. Green, and J. Q. Chambers, *ibid.*, **98**, 1596 (1976) (Part I).

(23) B. A. Scott, J. B. Torrance, S. J. LaPlaca, P. Corfield, D. C. Green, and S. Etemad, *Bull. Am. Phys. Soc.*, **20**, 496 (1975); S. J. LaPlaca, P. W. R. Corfield, R. Thomas, and B. A. Scott, *Solid State Commun.*, **17**, 635 (1975).

(24) F. B. Kaufman, J. B. Torrance, and Y. Tomkiewicz, Abstracts 168th National Meeting of the American Chemical Society, Atlantic City, New Jersey, September 1974; No. ORGN 47.

(25) (a) K. H. Hausser and J. N. Murrell, *J. Chem. Phys.*, **27**, 500 (1957); (b) K. Kimura, T. Yamazaki, and S. Katsumata, *J. Phys. Chem.*, **75**, 1768 (1971); (c) J. H. Fuhrop, P. Wasser, D. Riesner, and D. Mauzerall, *J. Am. Chem. Soc.*, **94**, 7997 (1972).

(26) R. H. Boyd and W. D. Phillips, *J. Chem. Phys.*, **43**, 2927 (1965); M. Itoh, *Bull. Chem. Soc. Jpn.*, **45**, 1947 (1972); J. J. Andre and G. Weill, *Chem. Phys. Lett.*, **9**, 27 (1971).

(27) (a) K. Takemoto, S. Nakayama, K. Suzuki, and Y. Ooshika, *Bull. Chem. Soc. Jpn.*, **41**, 1974 (1968); (b) K. Kimura, H. Yamada, and H. Tsubomura, *J. Chem. Phys.*, **48**, 440 (1968).

(28) S. Nakayama and K. Suzuki, *Bull. Chem. Soc. Jpn.*, **46**, 3694 (1973).

(29) Cf. ref 28, Figure 3; the concentration should be 1.16 × 10^{-4} mol/l.

(30) Y. Oohashi and T. Sakata, *Bull. Chem. Soc. Jpn.*, **46**, 765 (1973).

(31) (a) G. L. Levinson, W. T. Simpson, and W. Curtis, *J. Am. Chem. Soc.*, **79**, 4314 (1957); W. West and S. Pearce, *J. Phys. Chem.*, **69**, 1894 (1965). (b) E. A. Chandross, J. Ferguson, and E. G. McRae, *J. Chem. Phys.*, **45**, 3546 (1966).

(32) P. Mukerjee and A. K. Ghos, *J. Am. Chem. Soc.*, **92**, 6419 (1970); W. West, S. P. Lowell, and W. Cooper, *Photogr. Sci. Eng.*, **14**, 52 (1970); T. Nogami, K. Yoshihara, and S. Nagakura, *Bull. Chem. Soc. Jpn.*, **45**, 122 (1972).

(33) Apparently this holds true for the three species of dimers, since changing the identity of a large excess of counter anion affects neither the stoichiometry nor the thermodynamic parameters of the dimerization (cf. ref 28).

(34) A. Kawamori, A. Honda, N. Joo, K. Suzuki, and Y. Ooshika, *J. Chem. Phys.*, **44**, 4363 (1963).

(35) F. B. Kaufman and Y. Tomkiewicz, unpublished results.

(36) R. W. Taft, I. R. Fox, and I. C. Lewis, *J. Am. Chem. Soc.*, **83**, 3349 (1961).

(37) D. J. Williams and R. Kreilick, *J. Am. Chem. Soc.*, **90**, 2769 (1968).

(38) K. Watanabe, J. Yamauchi, H. Ohya-Nishiguchi, and Y. Deguchi, *Bull. Chem. Soc. Jpn.*, **47**, 274 (1974).

(39) D. I. Schuster, G. R. Underwood, and T. P. Knudsen, *J. Am. Chem. Soc.*, **93**, 4304 (1971).

(40) (a) R. Foster and C. A. Fyfe, *J. Chem. Soc. B*, 926 (1966); (b) I. Morishima, T. Inubushi, K. Endo, T. Yonezawa, and K. Goto, *J. Am. Chem. Soc.*, **94**, 4812 (1972).

(41) N. D. Epiotis, *J. Am. Chem. Soc.*, **95**, 3188 (1973).

(42) K. Fukui, T. Yonezawa, and C. Nagata, *J. Chem. Phys.*, **27**, 1247 (1957); *ibid.*, **31**, 550 (1959).

(43) M. A. Ratner and F. B. Kaufman, unpublished results.

(44) T. Sakata and S. Nagakura, *Bull. Chem. Soc. Jpn.*, **43**, 2414 (1970).

(45) For TMPD dimers, the most important steric interactions would involve the methyl-group hydrogens (CH_3–N(1)) and the edge carbons (C(3′),C(5′)) on the adjacent cation radical. The molecular models show that these interactions should be minimized, since they would require the involvement of intramolecular high-energy eclipsed hydrogen configurations between the methyl-group hydrogens (CH_3–N(1)) and the H atoms on the neighboring carbons C(2) and C(6). However, it should also be pointed out that an indirect type of steric effect, via changes in van der Waals distances, could result from rehybridization at the nitrogen atoms or ring carbons as a function of substitution. As previously discussed, the loss of methyl substituents in these systems leads to spin-density distributions, indicating increased contributions from quinoidal resonance forms II and III. These structures can be expected to have shorter van der Waals distances than the benzenoid forms I, but it is difficult to estimate how important this electronically induced steric effect is in these systems.

(46) Both bromides are orthorhombic with *Cmcm* space group. Unit-cell dimensions (cf. ref 9,10) are, $TMPD\cdot^{+}Br^{-}$: $a = 9.54$, $b = 19.27$, $c = 7.03$ Å. $DMPD\cdot^{+}Br^{-}$: $a = 6.38$, $b = 22.48$, $c = 6.21$ Å.

(47) J. Tanaka, M. Inoue, M. Mizuno, and K. Horai, *Bull Chem. Soc. Jpn.*, **43**, 1998 (1970).

(48) A. V. Sabitskii and M. Kutzenov, *J. Struct. Chem.*, **12**, 391 (1971).

(49) Cf. footnotes *i* and *j* in Table V.

(50) M. Ohmasa, M. Kinoshita, M. Sano, and H. Akamatu, *Bull. Chem. Soc. Jpn.*, **41**, 1998 (1968).

(51) W. D. Grobman, R. A. Pollack, D. E. Eastman, E. T. Maas, and B. A. Scott, *Phys. Rev. Lett.*, **32**, 534 (1974).

(52) J. B. Torrance, B. A. Scott, and F. B. Kaufman, *Solid State Commun.*, **17**, 1369 (1975).

(53) F. Denoyer, F. Comés, A. F. Garito, and A. J. Heeger, *Phys. Rev. Lett.*, **35**, 445 (1975).

Absolute Configuration of an Ansa Compound: Gentisic Acid Nonamethylene Ether[1]

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Abstract: The absolute configuration of gentisic acid nonamethylene ether is determined by a chemical correlation method. The levorotatory isomer is concluded to have the *S* configuration.

The determination of the absolute configuration of a variety of cyclophanes have been reported in recent years.[2] Three general methods have been used: (1) the interpretation of the stereochemical course of an asymmetric synthesis. This has included the treatment of a racemic cyclophane anhydride with a limited quantity of (−)-α-phenylethylamine and the reaction of an optically active alcohol, derived from an optically active cyclophane, with an excess of racemic α-phenylbutyric anhydride. (2) A comparison of NMR chemical shifts of diastereomeric cyclophanes. (3) A correlation of the sign of the ^1L_b Cotton effect of the benzene chromophore with the absolute configuration.