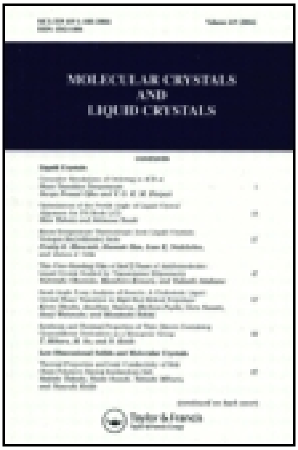


Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

Electrical Conductivity in TCNQ Salts of Bis(4-dimethylaminophenylimino) sulfur and its Structural Analogues

Martin L. Kaplan [a] , Robert C. Haddon [a] , Krishnan Raghavachari [a] , Shalini Menezes [a] , Frederic C. Schilling [a] , Jacques J. Hauser [a] & James H. Marshall [a]

[a] Bell Laboratories, Murray Hill, New Jersey, 07974

Version of record first published: 14 Oct 2011.

To cite this article: Martin L. Kaplan , Robert C. Haddon , Krishnan Raghavachari , Shalini Menezes , Frederic C. Schilling , Jacques J. Hauser & James H. Marshall (1982): Electrical Conductivity in TCNQ Salts of Bis(4-dimethylaminophenylimino) sulfur and its Structural Analogues, Molecular Crystals and Liquid Crystals, 80:1, 51-66

To link to this article: http://dx.doi.org/10.1080/00268948208071021

Mol. Cryst. Liq. Cryst., 1982, Vol. 80, pp. 51-66
0026-8941/82/8004-0051$06.50/0

Printed in the United States of America

Electrical Conductivity in TCNQ Salts of Bis(4-dimethylaminophenylimino) sulfur and its Structural Analogues

MARTIN L. KAPLAN, ROBERT C. HADDON, KRISHNAN RAGHAVACHARI, SHALINI MENEZES, FREDERIC C. SCHILLING, JACQUES J. HAUSER and JAMES H. MARSHALL

Bell Laboratories, Murray Hill, New Jersey 07974

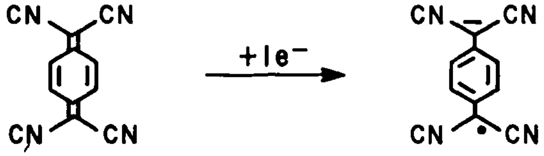
(Received June 26, 1981; in final form September 29, 1981)

Four compounds, *N,N,N',N'*-tetramethyl-*p*-phenylene diamine, *N,N,N',N'*-tetramethyl-benzidine, 4,4'-bis(dimethylamino)azobenzene and bis(4-dimethylaminophenylimino)sulfur (BAPIS) were examined electrochemically and spectroscopically. Each was shown to be a fairly good donor forming in its first oxidation state a radical-cation. The latter two materials surprisingly exhibited only single one-electron oxidations. Conformational flexibility about the -NSN- unit was studied by NMR spectroscopy and *ab initio* molecular orbital theory. The experimental ΔG^* for a cis-trans to trans-cis interconversion in BAPIS was found to be 11.9 kcal/mole.

The four donors all form 1:1 adducts with TCNQ. The compaction resistances of the complexes have been measured as a function of temperature. Of the four, (BAPIS)(TCNQ) appears to be a one-dimensional material. The other three complexes behave as typical mixed stack organic semiconductors.

INTRODUCTION

Organic charge-transfer salts of various donors and acceptors have received considerable attention due largely to observations of high electrical conductivity and unusual optical and magnetic properties in the solid state.[1] One acceptor molecule which has been the recipient of an inordinate share of scrutiny is 7,7,8,8-tetracyanoquinodimethane (TCNQ).[2] Reasons for this interest are intimately related to the combination of properties that are exhibited by TCNQ. For example, TCNQ is easily reduced in solution thereby forming a very stable, planar radical-anion (first reduction at +0.18v vs. SCE.[3] in acetonitrile) capable in the solid state of



forming molecular stacks with uniform spacings.[1] This ease of reduction has been an important factor in the preparation and study of the myriad well-known charge-transfer (CT) compounds that are extant (e.g. TTF-TCNQ,[4] NMP-TCNQ,[5] TTT-TCNQ,[6] TTN-TCNQ[7] etc.).

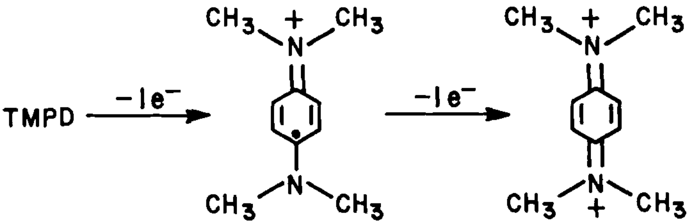
In many cases the mere mixing of solutions of the neutral donor and neutral TCNQ results in the formation of nicely crystalline CT compounds. In some instances metathetical reactions[8] of donor and acceptor salts are required to achieve well-formed crystals, or resort must be had to slow diffusion methods,[9] electrochemistry[10] or other esoterica.

In the present work our objective was to retain TCNQ as the acceptor in the study of a series of donor-acceptor (DA) compounds wherein the family of donors were chemically related. The choice of donors was made on the basis that their properties would be similar but that each succedent material would exhibit some sequential structural variation. The compounds thus selected were more or less linear and each had two dimethylamino groups substituted in the para positions of benzene rings. The smallest of the molecules, *N,N,N',N'*-tetramethyl-*p*-phenylene-diamine (TMPD), was the prototype of the other members of the group. In order of increasing size the other molecules studied were *N,N,N',N'*-tetramethylbenzidine (TMBZ), 4,4'-bis(dimethylamino)azobenzene (BDAA) and bis(4-dimethylaminophenylimino)sulfur (BAPIS). While looking at these donors we expected to gain additional information on the vagaries of the —NSN— unit. The properties of these donors have been examined and the compounds each makes with TCNQ has been prepared and studied.

RESULTS AND DISCUSSION

1. Properties of Donors

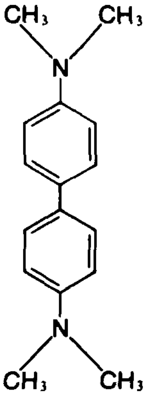
The compound TMPD is well known as the precursor to Wurster's Blue (WB) radical cation. This species forms upon



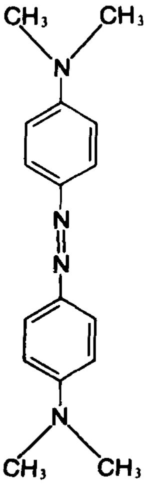
WB

$TMPD^{++}$

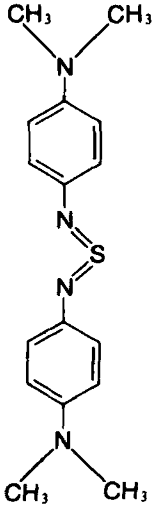
one-electron oxidation of the neutral compound.[11] A second one-electron oxidation is also known to occur, resulting in the TMPD dication. Interposition of additional conjugative groups between the dimethylamino units permits molecules with essentially similar oxidative behavior to exist. Therefore, when TMBZ, BDAA and BAPIS are subjected to oxidizing conditions the first one-electron loss should result in the formation of a radical cation, and the second a dication. Many factors may influence the ease of oxidation of donors, e.g. TMBZ is a worse donor than TMPD (for the first oxidation) because of the lack of coplanarity of the benzene rings in TMBZ.



TMBZ



BDAA



BAPIS

To be considered, as these molecules get larger and larger, is the fact that the number of contributing structures that can be drawn for the mono and divalent species increases dramatically, thereby enhancing resonance stabilization. In addition, the larger the molecules, the easier it should be to get to the dication

TABLE I

Values Obtained from Levich Experiment for the Number of Electrons per Donor Oxidation Wave and Cyclovoltammetric Results

Curve No.	Compound	conc mM	E v vs. SCE	ma rpm$^{-1/2}$	$i_L/\omega^{1/2}$ n	E_1[a]	
1a	TMPD	0.2_5	0.5	2.8×10^{-4}	0.92	0.17	0.76
1b			1.0	5.5×10^{-4}	1.81		
2	BAPIS	0.2_2	0.5	3.1×10^{-4}	1.16	0.42	
3	BDAA	0.2_2	0.8	3.3×10^{-4}	1.23	0.63	
	TMBZ					0.47	0.66

[a] Obtained in acetonitrile using 0.1 M tetra-*n*-butylammonium tetrafluoborate as supporting electrolyte with a Pt working electrode vs. SCE.

stage because of minimization of Coulombic repulsions. To examine this point, cyclic voltammetry on the four compounds has been performed (Table I). As expected, TMPD and TMBZ exhibit two reversible one-electron oxidation waves, and the second wave of the latter occurs at 0.1V lower than that for the former. Quite unexpectedly only single reversible waves were found for BDAA and BAPIS, even when sweeping as far as +1.5V.

The question then arose as to the number of electrons actually being transferred in these single waves. Although coulometry could have been used we chose the experimentally straightforward method described below. The number of electrons, n, in the convective-diffusion limited oxidation of a reduced species of concentration C and diffusion coefficient D, at a disk electrode of area A rotating at speed ω is given by the Levich equation,[12]

$$n = \frac{1.61\, i_L \nu^{1/6} D^{-2/3} \omega^{1/2}}{\mathrm{FAC}}$$

where i_L is the limiting current, ν the kinematic viscosity and F the Faraday constant. In the convective-diffusion controlled process, n can be estimated from the slope of the Levich plots of i_L against $\omega^{1/2}$. Programming $\omega^{1/2}$ as a function of time permits recording i_L vs. $\omega^{1/2}$ plots rapidly and has proved useful in studying the reaction mechanisms of unstable or air sensitive species.[13]

Such experiments were performed with TMPD, BAPIS and BDAA with the electrode potential held at the limiting current step of the oxidation curve, i_L was monitored as $\omega^{1/2}$ and was continuously increased. Plots of these data resulted in straight lines. The slopes of the curves together with concentration data are listed in Table I. The variation in the slopes of curves 1(a), 2 and 3 are within the error limits of the experiment and indicate that BAPIS and BDAA oxidations involve the same number of electrons as does the first wave for TMPD. Slope 1(b) is approximately twice that for 1(a), 2 and 3, suggesting

TABLE II

Geometrical Parameters involving *S* in sulfur di-imide isomers obtained with the STO-3G* basis

		Geometrical Parameter	
	N S	N S	
	1	2	
	0	0	NSN
Structure	(A)	(A)	(Degrees)
1	1.526	1.526	122.6
2	1.523	1.538	115.6
3	1.537	1.537	110.9
4	1.528	1.506	119.4
5	1.524	1.456	120.5
6	1.539	1.504	114.9
7	1.540	1.452	114.6

that twice as many electrons are involved. Using literature values of 2.33×10^{-5} cm^2 sec^{-1} for ν[15] we computed values of *n*, as shown in Table I. Inaccuracies in the choice of *D* or in measurement of *C* (due to solvent evaporation, etc.) may explain the magnitude of the errors of ±0.2 electrons found for *n*. Nevertheless, these data clearly show that BAPIS and BDAA oxidize by one-electron processes.

That BDAA and BAPIS form radical-cations was demonstrated by the solution esr spectra obtained from chemically oxidized material. The BAPIS spectrum was obtained in propylene carbonate with $HClO_4$ and the BDAA spectrum in nitrobenzene with I_2. The complexity of the spectra precluded any simplified analysis.[16] However, the *g*-value for BAPIS of 2.0029 may imply that little if any spin is delocalized onto the sulfur. The *g*-value for BDAA is similar at 2.0026.

One of the complicating factors which became apparent in the course of our work was the variety of structural isomers that can exist, both with BDAA and BAPIS. For example, previous workers[17] have studied the ^1H NMR spectra at several temperatures of simple alkylated sulfur diimides and considered the contributions of the three possible geometric isomers, **1**, **2** and **3**. They showed that at low temperature, (−40°C) the single line observed for dimethylsulfurdiimide at 25°C becomes three resonances, two lines of equal intensity (A_3B_3) and a smaller singlet at lower field. They interpreted these results as being caused by the presence of two isomers. The cis, trans compound, they reasoned, was responsible for the A_3B_3 system and the small singlet due to the (trans, trans). The di-*t*-butylsulfurdiimide spectrum split, at low temperature, into two equal singlets due to the cis, trans material. The stability of the (cis, trans) configuration has been shown by CNDO calculations[18] and by X-ray crystallographic structure analysis of di-*p*-tolylsulfurdiimide.[19]

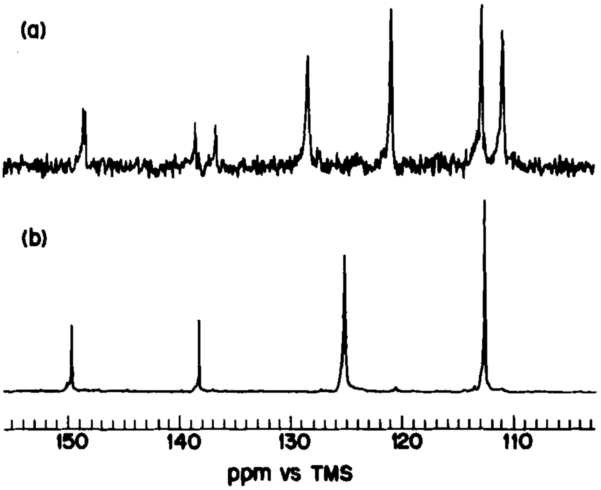
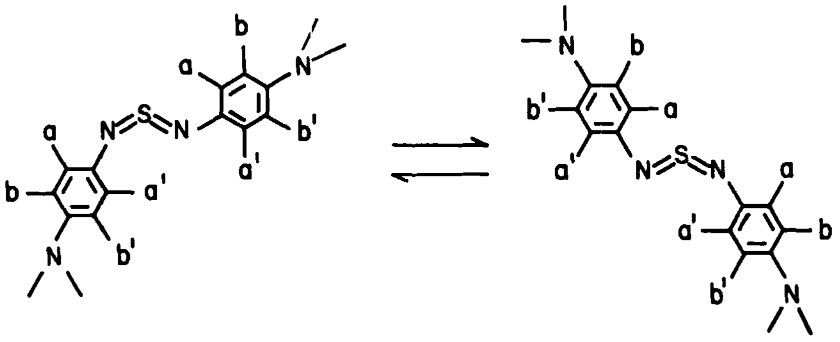


FIGURE 1 22.62 MHz ^{13}C NMR spectra for BAPIS at (a) −101°C and (b) +35°C. Only the aromatic region is shown.

The preparation and NMR spectroscopy of a number of diaryl sulfurdiimides, including ^{1}H NMR for BAPIS, has previously been reported.[20] At low temperatures, in most cases, two isomeric forms were believed to exist, the (cis, trans) being the most abundant and the (trans, trans) the least. BAPIS according to these authors existed only as (cis, trans). We have carefully reexamined both the ^{1}H and ^{13}C (Figure 1) NMR spectra of BAPIS. At 24°C the proton spectrum appears as a typical AA′BB′ pattern of two doublets, one at δ6.63 and one at δ7.13.



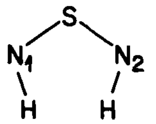
What we assign as the B protons occur at δ6.63 which compares well with the chemical shift found for the orthohydrogens in *N,N*-dimethylaniline of δ6.67.[21] As the temperature is lowered the spectrum changes. Both the A and B protons split into pairs of doublets. The A protons, those closest to the NSN group, are affected most by lowering of the temperature. If only the (cis-trans) isomer were present, the ratio of the areas of the downfield AA′ doublets should be one. What is found, however, is a temperature dependent variable ratio. For example, at −60° the highfield A/lowfield A ratio is 1.6:1, while at −83° it is 1.2:1. The implication here is that at the same chemical shift as the upfield A hydrogens are the A hydrogens of another isomer (all trans or all cis) at approximately 1/5 the concentration.

The ^{13}C spectra are consistent with this interpretation. At +35°C the aromatic region shows four different carbons, two quaternary and two protonated. We assign the low field line (150 ppm) to the carbon attached to the *N,N*-dimethyl group and the high field line (112.8 ppm) to the carbon adjacent to the *N,N*-dimethyl group. This compares to 151.3 ppm and 113.1 found for the analagous carbons in *N,N*-dimethylaniline.[22] As the temperature is lowered all the lines split into two. The protonated carbons at 125 ppm adjacent to the NSN link are affected most by the slowing of the isomerization process and consequently separate the farthest. The ratio of the intensities of the two lines that result at −101°C is approximately 1.2:1. The lines resulting from the other protonated carbon exhibit a similar intensity ratio.

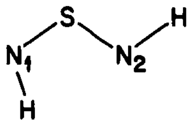
Also, from the proton spectra coalescence temperature of −21°C, a ΔG^* for conformational isomerization can be deduced. The residence time, τ, was calculated[23] from, $\tau = \sqrt{2}/2\pi\Delta\nu$, where $\Delta\nu$ is the maximum reference peak separation of 98 Hz. Substitution of the rate constant, $\frac{1}{2}\tau$, in the Eyring formulation gives a value of $\Delta G^* = 11.9$ kcal/mole.

2. Theoretical Investigations of the Conformational Processes in Sulfur Diimide

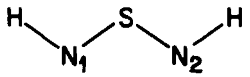
In order to investigate the conformational flexibility about the —NSN— unit, *ab initio* molecular orbital calculations have been carried out to obtain the barriers of interconversion between various isomers of the parent sulfur diimide. The three isomers (cis, cis) 1, (cis, trans) 2 and (trans, trans) 3 have been considered. Both rotation and inversion pathways about *N* were considered as possible interconversion mechanisms between 2 and 1 and between 2 and 3. This results in the following transition state structures 4–7.



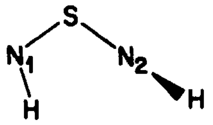
1 (C_{2v})



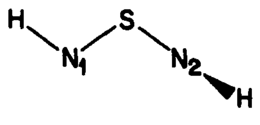
2 (C_s)



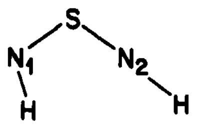
3 (C_{2v})



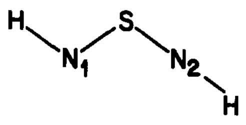
4 (C_1)



6 (C_1)



5 (C_s)



7 (C_s)

4 and 5 are the rotation and inversion transition structures respectively for the interconversion between 2 and 1. 6 and 7 are the corresponding transition structures for the interconversion between 2 and 3. These structures have been considered previously at the CNDO level by Grunwell and Danison.[18] Our calculations employ a more sophisticated level of theory and the results are significantly different.

An inspection of the geometrical parameters listed in Table II reveals that the geometries are in good agreement with experimental data for the dimethyl derivative. For example, the N—S bond lengths (1.523 and 1.538 Å) and the N—S—N bond angle (115.6) in 2 agree well with the experimental (electron diffraction data[24]) bond length of 1.532 Å (both bond lengths assumed equal) and bond angle of 113.6. Another notable feature in Table II is that in all the transition structures 4–7, the N_2—S bond length (the bond length involving the rotating or inverting *N*) is shorter than in the regular structures 1–3. This indicates that multiple bonding character exists and is even strengthened in these transition structures. Detailed discussion of this effect will be given elsewhere.[25]

The total and relative energies at the final MP2/6-31G* level are listed in Table III and compared with the relative energies found by the CNDO calculations.[18] The cis, cis form 1 is found to be of lowest energy being slightly (1 kcal/mol) more stable than 2. The trans, trans form is considerably higher in energy (5·2 kcal/mol less stable than 2). Inspection of the pair of structures 4 and 5 and the pair 6 and 7 reveals that within each isomerization reaction, the rotation is a slightly lower energy path than inversion. Use of the larger 6-31G* basis lowers all the barriers by about 7 kcal/mol. The final relative energies indicate that cis, trans to cis, cis interconversion involves a lower bar-

TABLE III

Total and relative energies of the various sulfur di-imide isomers

Structure	MP2/6-31G* Total Energy (Hartrees)	CNDO[18] Relative Energy (kcal/mol)	
1	−507.93593	−1.0	1.95
2	−507.93440	0.0	0.0
3	−507.92614	5.2	4.52
4	−507.90608	17.8	12.99
5	−507.90327	19.5	4.20
6	−507.90032	21.4	10.23
7	−507.89576	24.2	1.25

rier than cis, trans to trans, trans interconversion and that rotation is the preferred pathway (though only slightly). Hence if we consider the interconversion of the cis, trans isomer to the trans, cis form the barrier is 17 • 8 kcal/mol and the process involves the cis, cis compound as an intermediate. These results differ significantly from the CNDO results[18] (Table III) and hence detailed comparisons between the two calculations will not be attempted.

Similar calculations are in progress for the dimethyl sulfur diimide compound. An obvious result of the methyl or larger group substitution would be to lower the relative stability of the cis, cis compound due to steric effects. This would be in accord with the significantly lower barrier reported above for the *N,N*-dimethylamino phenyl derivative.

3. Properties of TCNQ Complexes

When warm solutions of the neutral donors TMPD, TMBZ, BDAA and BAPIS were mixed with warm solutions of TCNQ immediate darkening of the mixtures occurred and black crystalline products were formed. The TMPD-TCNQ previously prepared in this manner was shown to be a 1 : 1 complex.[11] Its crystal structure[26] has been determined and consists of mixed chains of donor and acceptor molecules. The complex salt (TMPD)$(TCNQ)_2$ has also been prepared [11,27] and its crystal structure[27] shown to differ from that of the simple salt, in that it is made up of segregated stacks of donors and acceptors. Highly conducting quasi-one-dimensional systems have as a prime requisite such segregated stacks in addition to small, uniform spacings within the stacks.[1] A comparison of the conductivities of compactions of (TMPD)(TCNQ) and (TMPD)$(TCNQ)_2$ indeed showed the complex salt to have a much higher conductivity.[11]

In a like manner, we have studied the compaction conductivities of the TCNQ complexes of TMBZ, BDAA, and BAPIS all of which were shown to be simple salts by elemental analysis. A comparison of the conductivity data is presented in Figure 2. The (TMPD)(TCNQ) data comes from Ref. 11.

The values of the measured resistances might not reflect a true absolute value as would be the case in single crystal four-probe measurements. These limitations no doubt reflect problems of interparticle tunneling, and potential barriers. Nevertheless, we are confident that the obtained activation energies are a true measure of the conduction mechanism.

The three compounds, (TMPD)(TCNQ), (TMBZ)(TCNQ) and (BDAA)(TCNQ) all exhibit a temperature dependence of their electrical resistivity consistent with typical Arrhenius behavior, i.e. $\rho = \rho_0 \exp(-E_a/kT)$. The activation energies determined are shown in Figure 2 and are typical of values obtained for other TCNC based solids. Attempts to fit (BAPIS)(TCNQ) to this model were not successful. Alternatively, the straight line plot of the resistance of a conductor against $T^{-1/2}$ has been shown to be indicative of structurally disordered one-dimensional compounds. The equation[28] describing such a system is $\ln \sigma \sim -|T_0/T|^{1/2}$ (σ = conductivity, T = temperature, and T_0 = energy term) and when used with our data give a straight line fit for (BAPIS)(TCNQ). A measure of the activation energy (T_0) was calculated to be 1.2×10^5 °K which is higher than that found for other simple organic salts of TCNQ, e.g. (NMP)(TCNQ),[29] $T_0 = 1.72 \times 10^4$ °K; (TTF)(TCNQ)[30], $T_0 = 4.1 \times 10^3$ °K. These results suggest strongly that while (BAPIS)(TCNQ) belong to that class of highly anisotropic disordered materials it has the greatest barrier to electrical conduction yet observed.

Reasons for this effect depend on the solid state structure of the salt.[31] It is not unreasonable to expect that the crystal structure will show the typical uniform stacks of TCNQ molecules as found in other one-dimensional materials, and that these stacks will be the dominant factor in the conduction mechanism. It has been reported that optical spectra can be used to ascertain charge transer band energies and hence information regarding the TCNQ aggregates.[1b] When we attempted such measurements we obtained broad featureless spectra, perhaps due to interference by radical cation absorption.

The BAPIS molecules, because of their inherent character, may form highly disordered chains thereby limiting their ability to transmit electronic charge. The picture we propose for the solid state structure of (BAPIS)(TCNQ) inculpates the BAPIS moiety as responsible, because of (1) its high degree of conformational flexibility as a neutral and charged species; (2) its large number of electronically equivalent resonance contributors; and, (3) its inability to form a dication, for its relatively poor conductivity behavior.

We note also, that at least for the three simple salts considered here, there appears to be some correlation between the activation energy for conduction and (1) donor oxidation potential, and (2) donor length. These crude curves, (Figure 3) are shown only to illustrate a trend, and not to imply the existence

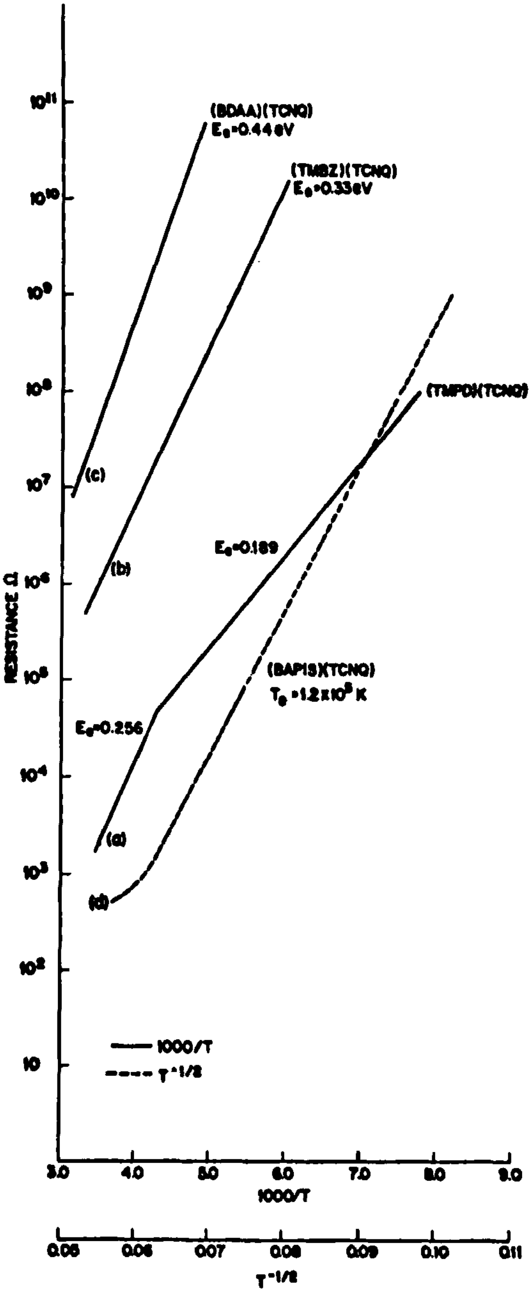


FIGURE 2 Comparison of Resistancies of Compactions of Various TCNQ Salts as a Function of Temperature.

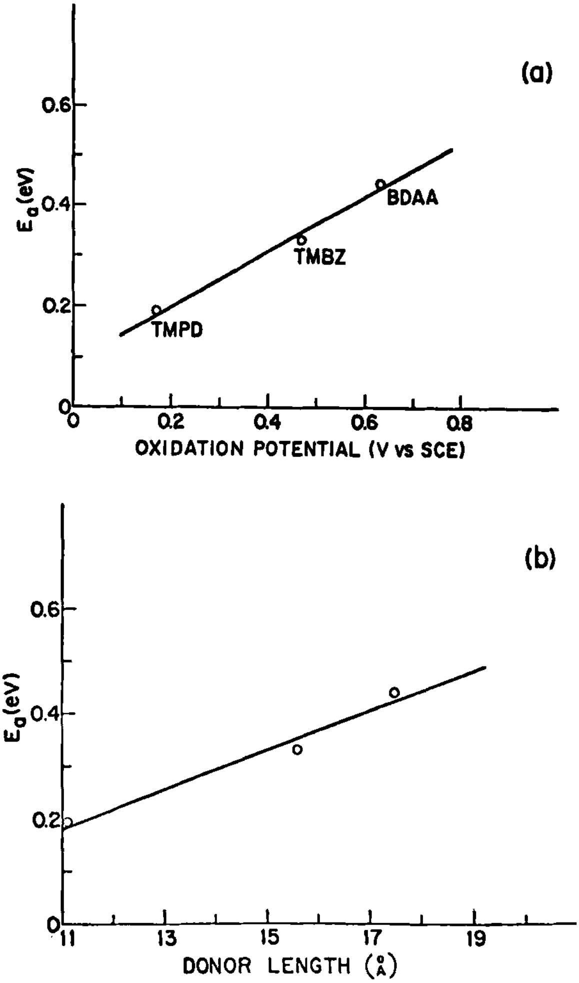


FIGURE 3 Energy of Activation of (DA) Conductivity as a Function of (a) donor oxidation potential and (b) donor length.

of any precise mathematical relationship. The oxidation potentials were obtained from our cyclic voltammetry measurements. Donor lengths were obtained from simple end-to-end measurements of appropriate molecular models. The progression observed might have been predicted on the basis that the larger and more disordered the cation, the larger the number of microscopic defects and thus the greater the number of random potentials. This effect would cause and increase in the activation energy for conduction as would the poorer packing in the crystal that could arise from progressively differing size of cation versus anion.

CONCLUSIONS

The donor properties of four compounds possessing bis(dimethylamino) group substitution have been examined. Electrochemical oxidation and ESR experiments showed that TMPD, TMBZ, BDAA and BAPIS oxidize readily and form radical cations on one-electron removal. TMPD and TMBZ can be further oxidized, by removal of a second electron, thus forming dications. However, BDAA and BAPIS do not exhibit such a second oxidation step probably due to the high stability of the initially formed radical cations.

All four donors form 1 : 1 adducts with TCNQ. The compaction resistances of the complexes have been measured as a function of temperature. The data for (BAPIS)(TCNQ) suggest that this material is highly anisotropic, and even one-dimensional. The other three complexes behave as typical mixed stack organic semiconductors in which the activation energy for conductivity increases as donor length increases.

Conformational flexibility about the —NSN— unit in BAPIS was studied by NMR spectroscopy. Both ^1H and ^{13}C were measurements consistent with an explanation that two isomers exist at low temperatures. *Ab initio* molecular orbital calculations have been carried out on the parent sulfur diimide and indicate that the trans-trans isomer is considerably less stable (5.2 kcal/mole) than the cis-trans isomer, and that the cis-cis isomer is slightly more (1 kcal/mole) stable. The interconversion of cis-trans forms is calculated to proceed via cis-cis and involves a barrier of 18 kcal/mole.

EXPERIMENTAL AND CALCULATIONAL

1. Materials

TMPD, TMBZ and TCNQ were commercially available and recrystallized before use. BDAA was prepared by $Ag^{II}O$ oxidation of *N,N*-dimethyl-*p*-phenylenediamine.[32] BAPIS was synthesized from *N,N*-dimethyl-*p*-phenylenediamine and SF_4^{20} or by reaction of *p*-dimethylaminothionylaniline with K-*t*-butoxide/DMF.[33]

Donor-Acceptor Salts The preparation of (BAPIS)(TCNQ) is illustrative of the syntheses of all the compounds studied here.

A solution of TCNQ (0.10 g, 4.9×10^{-4} moles) in hot, dry (silica gel) acetonitrile (40 mL) was added to a hot solution of BAPIS (0.15 g, 5×10^{-4} moles) in acetonitrile (10 mL). The flask was wrapped in insulating paper and then permitted to stand 16 hrs. at room temperature. The black, shiny, metallic needles were collected by filtration, washed with toluene and ether then dried under N_2. The yield was 0.13 g (53%). Anal. Calc. for $C_{28}H_{24}N_8S$: C, 66.65; H, 4.79 N, 22.21. Found: C, 66.38; H, 5.05; N, 22.29 Yield of

(TMBZ)(TCNQ)—73% Anal. Calc. for $C_{28}H_{24}N_6$: C, 75.65; H, 5.44; N, 18.91. Found: C, 76.25; H, 5.74; N, 18.94. (BDAA)(TCNQ)—Anal. Calc. for $C_{28}H_{24}N_8$: C, 71.17; H, 5.12, N, 23.71. Found: C, 70.81; H, 5.29; N, 23.56.

2. Electrochemistry

Cyclic voltammetry was carried out in distilled acetonitrile (from P_2O_5) with 0.1 M *n*-Bu_4NBF_4 as supporting electrolyte, with a platinum working electrode and SCE reference. All measurements were performed at ambient temperatures (22°C) on approximately 10^{-3} M solutions of substrate.

The Levich experiment[12] utilized a platinum disk of 0.317 cm^3 area in an epoxy insulated mantle. A three electrode cell consisting of an SCE reference and platinum counter electrode was operated potentiostatically under an atmosphere of nitrogen. Linear potential scans were recorded at 1600 rpms. The programmed speed control has been previously described.[13] Solutions were prepared from *n*-Bu_4NBF_4 and the various donors in distilled acetonitrile.

3. NMR Spectroscopy

^{13}C spectra were recorded on a Bruker WH-90 FT spectrometer operating at 22.62 MHz with sample temperatures varied between +35° to −101°C. Sample concentrations were 10% w/v and contained TMS as reference. At −101° the solvent was CD_2Cl_2/CS_2 and a ^1H decoupled spectrum required accumulation of 100 scans at a 2.0 sec. repetition times using 13 μs, 90° pulses with a 5000 hz sweep width in 8K data points. At +35°C CD_2Cl_2 was used as solvent. The spectra was obtained by accumulating 7650 scans at a 30.0 sec. repetition time using 13 μs, 90° pulses with a 4000 hz sweep width in 8K data points.

^1H spectra were obtained on a Bruker WH-90 spectrometer on 5% w/v solutions. The solvent was CD_2Cl_2 which was also the secondary reference (5.30 ppm vs. TMS). Recording conditions were, 25 scans with a sweep width of 600 hz in 4K data points at 3.5 sec. repetition time with 0.1 μs pulses.

4. Conductivity Measurements

Standard two probe resistance measurements were performed on compacted powders. Dimensions of the final pellet were 0.125″ diameter by 0.040″ thickness.

5. Computation

Ab initio molecular orbital theory was used throughout. Preliminary geometry optimizations were carried out using the minimal STO-3G basis.[34] However, this basis set was found to be inadequate in describing the bonding in these compounds, especially the transition structures. Hence the larger STO-3G[35] basis which has a set of 5 *d*-functions on *S* was used for all the geometries reported in this paper. This basis set is known to adequately describe the geometries and energies of second row compounds containing hypervalent bonding.[35–37] All the geometries were optimized completely within the given symmetry constraint and some of the interesting geometrical features are listed in Table II. A more complete description of the geometry and bonding in these compounds will be given in a future publication.[25] These geometries were then used in single point calculations with the larger 6-31G* basis (66-31G* for S).[38,39] This is a split valence basis with *d*-functions on both *S* and *N*. Electron correlation was included at the second-order Moller-Plesset perturbation level[40,41] with this basis (MP2/6-31G* level) to obtain final energy differences (listed in Table III). Only the valence electron correlation was evaluated in all cases. All the calculations were performed with the Gaussian 80 program[42] on a Cray-1 computer.

References

1. (a) I. F. Shchegolev, *Phys. Status Solidi*, **A12,** 9 (1972). (b) J. B. Torrance, *Accounts Chem. Res.*, **12,** 79 (1979). (c) A. F. Garito and A. J. Heeger, *Accounts Chem. Res.*, **7,** 232 (1974).
2. D. S. Acker and W. R. Hertler, *J. Am. Chem. Soc.*, **84,** 3370 (1962).
3. M. L. Kaplan, R. C. Haddon, F. B. Bramwell, F. Wudl, J. H. Marshall, D. O. Cowan and S. Gronowitz, *J. Phys. Chem.*, **84,** 427 (1980), see also ref. 2 for TCNQ electrochemistry.
4. J. P. Ferraris, D. O. Cowan, V. Walatka, and J. H. Perlstein, *J. Am. Chem. Soc.*, **95,** 948 (1973).
5. L. R. Melby, *Can. J. Chem.*, **43,** 1448 (1965).
6. (a) L. J. Buravov, O. N. Eremenko, R. B. Lyubovskii, L. P. Rosenberg, M. L. Khidekel, R. P. Shibaeva, I. F. Shcheyolev and E. B. Yaglibskii, *JETP Letters*, **20,** 208 (1974). (b) P. Delhaes, S. Flandrois and G. Keryer, *Mat. Res. Bull.*, **10,** 825 (1975).
7. F. Wudl, D. E. Schafer and B. Miller, *J. Am. Chem. Soc.*, **98,** 252 (1976).
8. F. Wudl, *J. Am. Chem. Soc.*, **97,** 1962 (1975).
9. M. L. Kaplan, *J. Crystal Growth*, **33,** 161 (1976).
10. F. B. Kaufman, E. M. Engler, D. C. Green and J. Q. Chambers, *J. Am. Chem. Soc.*, **98,** 1596 (1976).
11. R. Somoano, V. Hadek, S. P. S. Yen and A. Rembaum, *J. Chem. Phys.*, **62,** 1061 (1975).
12. V. G. Levich, "Physiochemical Hydrodynamics," Prentice-Hall, Englewood Cliffs, N.J. 1962, p. 65.
13. B. Miller, M. I. Bellavance and S. Bruckenstein, *Anal. Chem.*, **44,** 1983 (1972).
14. Bacon and R. N. Adams, *Anal. Chem.*, **42,** 524 (1970).
15. Handbook of Chemistry and Physics, CRC.
16. For the difficulties encountered with TMBZ$^{+\cdot}$ see: J. M. Fritsch and R. N. Adams, *J. Chem. Phys.*, **43,** 1887 (1965).
17. J. R. Grunwell, C. F. Hoyng and J. A. Rieck, *Tetrahedron Lett.*, 2421 (1973).
18. J. R. Grunwell and W. C. Danison, Jr., *Tetrahedron*, **27,** 5315 (1971).
19. G. Leandri, V. Busetti, G. Valle and M. Mammi, *J. Chem. Soc. Chem. Commun.*, 413 (1970).
20. J. Kuyper and K. Vrieze, *J. Organometal. Chem.*, **86,** 127 (1975).
21. H. Spiesecke and W. G. Schneider, *J. Chem. Phys.*, **35,** 731 (1961).
22. J. B. Stothers, "^{13}C NMR Spectroscopy" (Vol. 24 of Organic Chemistry Series), Academic Press, New York, 1972, p. 197.

23. J. A. Pople, W. G. Schneider and H. J. Bernstein, "High Resolution Nuclear Magnetic Resonance," McGraw-Hill, New York, 1959, p. 223.
24. J. Kuyper, P. H. Iselmann, F. C. Mijhoff, A. Spelbos and G. Renes, *J. Mol. Struc.*, **29**, 247 (1975).
25. K. Raghavachari and R. C. Haddon (to be published).
26. A. W. Hanson, *Acta Cryst.*, **19**, 610 (1965).
27. A. W. Hanson, *Acta Cryst.*, **B24**, 768 (1968).
28. A. N. Bloch, R. B. Weisman and C. M. Varma, *Phys. Rev. Letters*, **38**, 753 (1972).
29. V. K. S. Shante, C. M. Varma and A. N. Bloch, *Phys. Rev. B*, **8**, 4885 (1973).
30. J. J. Hauser, unpublished observations of compaction conductivity data.
31. X-ray Crystallographic Structure determination in progress, A. Gieren, V. Lamm, R. C. Haddon and M. L. Kaplan.
32. B. Ortiz, P. Villanueva and F. Walls, *J. Org. Chem.*, **37**, 2748 (1972).
33. H. H. Hôorhold and J. Beck, *J. Prakt. Chem.*, **311**, 621 (1969).
34. W. J. Hehre, R. F. Stewart and J. A. Pople, *J. Chem. Phys.*, **51**, 2657 (1969).
35. J. B. Collins, P. V. R. Schleyer, J. S. Binkley and J. A. Pople, *J. Chem. Phys.*, **64**, 5142 (1976).
36. M. S. Gordon, J. S. Binkley, J. A. Pople, W. J. Pietro and W. J. Hehre, *J. Chem. Phys.*, (to be published).
37. R. C. Haddon, S. R. Wasserman, F. Wudl and G. R. J. Williams, *J. Am. Chem. Soc.*, **102**, 6687 (1980).
38. P. C. Hariharan and J. A. Pople, *Mol. Phys.*, **27**, 209 (1974).
39. J. S. Binkley, W. J. Hehre and J. A. Pople (to be published).
40. C. Moller and M. S. Plesset, *Phys. Rev.*, **46**, 618 (1934).
41. J. S. Binkley and J. A. Pople, *Int. J. Quant. Chem.*, **9**, 229 (1975).
42. J. S. Binkley, R. A. Whiteside, R. Krishnan, R. Seeger, D. J. DeFrees, H. B. Schlegel, S. Topiol, L. R. Kahn and J. A. Pople; available from the Quantum Chemistry Program Exchange.