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Crystal and Molecular Structure and Properties of Picolyltricyanoquinodimethan, the Zwitterionic Donor-Pi- Acceptor Adduct Beiween $Li^{+}Tcnq^{-}$ and 1,2-Dimethyl-Pyridinium Iodide

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CRYSTAL AND MOLECULAR STRUCTURE AND PROPERTIES OF PICOLYLTRICYANOQUINODIMETHAN, THE ZWITTERIONIC DONOR-PI-ACCEPTOR ADDUCT BETWEEN LI^+TCNQ^- AND 1,2-DIMETHYLPYRIDINIUM IODIDE*

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Abstract: The reaction of the lithium salt of 7,7,8,8-tetracyanoquinodimethan (TCNQ) with 1,2-dimethylpyridinium iodide in ethanol leads to a conventional charge-transfer salt. However, the same reagents dissolved in acetonitrile yield crystals which belong to space group $P2_1/c$, with unit cell constants $\underline{a}$ = 1493.5(2), $\underline{b}$ = 720.9(2) (stack axis), $\underline{C}$ = 1380.2(3) pm, β = 107.06(2)°, Z = 4 for $C_{18}H_{13}N_4$. 1746 unique CAD-4F diffractometer Mo Kα data refined to R = 5.1 per cent, to yield the structure of the zwitterionic donor-pi-acceptor adduct Z-β-(N-methyl-2-pyridyl)-α-cyano-4-styryl dicyanomethide (trivial name: picolyl-tricyanoquinodimethan, P3CNQ). The pyridinium ring is inclined 30.13° from the quinodimethan 6-membered ring. The salt is diamagnetic, and the pyridinium N atom stacks above the dicyanomethide portion of the next molecule along the $\underline{b}$ axis.

INTRODUCTION

The potent organic π-acid (one-electron acceptor) 7,7,8,8-tetracyanoquinodimethan (TCNQ, Fig.1,I) has been known since 1960[1,2]: it forms charge-transfer salts with a great variety of electron donors.[3] As discussed elsewhere in

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these Proceedings, TCNQ forms several quasi-one-dimensional ''metallic'' electrical conductors, e.g. N-methylphenazinium TCNQ (NMP (Fig.1,II) TCNQ),[4] and tetrathiafulvalene (TTF (Fig.1,III)) TCNQ.[5,6] These and other related highly conducting materials have been studied intensively, as attested by review articles,[7-11] monographs, and meeting proceedings.[16-25]

The conventional substitution reactions of TCNQ (replacement of cyano groups by nucleophilic species) were originally described by the du Pont research of cyano group,[26] and they resemble the substitution reactions of tetracyanoethylene (TCNE, Fig.1,IV) which had been studied earlier.[27] The tricyanovinylamines (Fig.1,V) obtained[28-38] from the reaction of amines with TCNE have received considerable attention, while the analogous TCNQ derivatives like the 7-amino-7,8,8-tricyanoquinodimethans[26] (Fig.1,VI) have been ignored since 1962.

Covalently bonded σ-dimers of $TCNQ^-$ have been studied;[39-42] there is also considerable theoretical[43,44] and experimental[45-47] interest in D-σ-A compounds where a potent electron donor D is sigma-bonded to A, a potent electron acceptor like TCNQ.

One of us (GJA) has been studying the crystallographic, magnetic, and electrical conductivity properties of pyridinium and polypyridinium salts of TCNQ.[48-64] We present here a preliminary report on the synthesis, crystal structure, optical and magnetic properties of a novel molecular adduct, in which 1,2-dimethylpyridine, as the electron donor, has reacted with TCNQ to form a covalently bonded zwitterionic adduct $D^+-\pi-A^-$. In the reaction, HCN

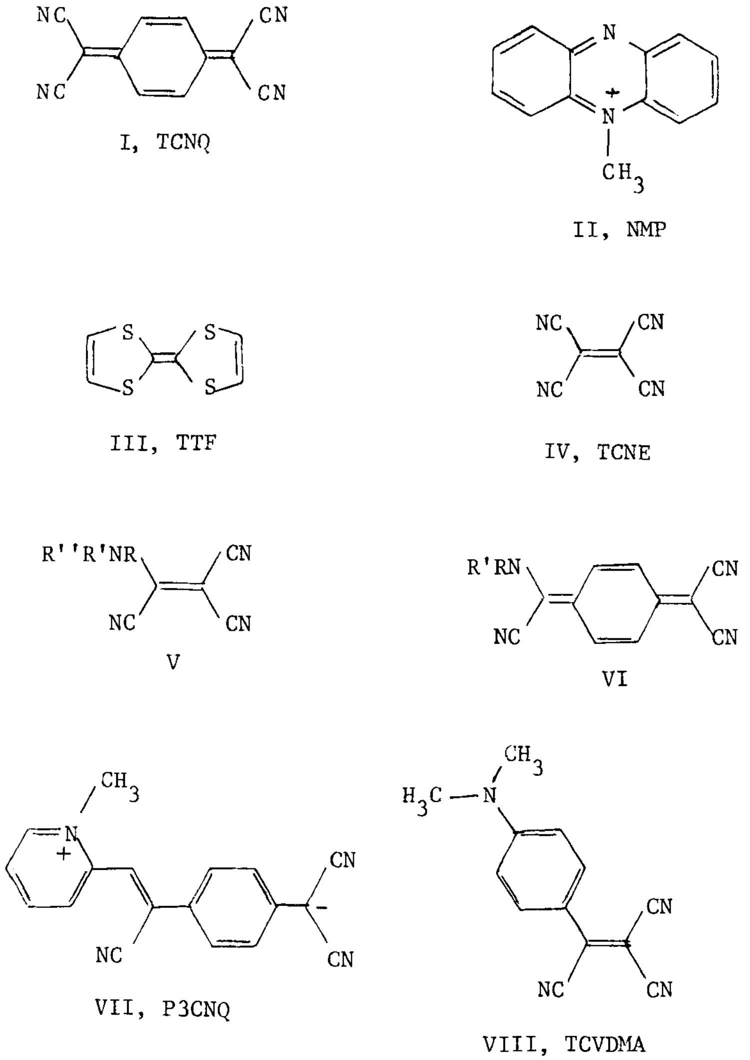

FIGURE 1.

has been lost, and the new molecule, Z-β-(N-methyl-2-pyridyl)-α-cyano-4-styryl dicyanomethide (Fig.1,VII) is a TCNQ analog of the tricyanovinylamines(V) mentioned above. We propose the trivial name picolyl-tricyanoquinodimethan and the acronym P3CNQ for molecule VII.

EXPERIMENTAL

Synthesis

The reaction of the lithium salt of TCNQ (Li^+TCNQ^-) with 1,2-dimethylpyridinium iodide ($Me_2Py^+I^-$) yields different products in ethanol and acetonitrile solutions.

A hot solution of 0.2 g of Li^+TCNQ^- in 50 mL of ethanol was added to a hot solution of 0.2 g of $Me_2Py^+I^-$ in 50 mL of ethanol. After the resultant green solution had cooled to room temperature, crystals (purple plates) of the ionic charge-transfer salt were obtained. The crystals (90% yield) were removed by filtration and washed with ethanol and with ether.

Elemental analysis: calculated (found) for $C_7H_{10}N^+C_{12}H_4N_4^-$: C, 73.05% (73.47)%; H, 4.52 (4.52); N, 22.43 (22.45). The UV-visible spectrum of the complex dissolved in ethanol showed the typical absorption spectrum of $TCNQ^-$ with peaks. at λ_{max} = 420 and 842 nm.

A hot solution of 0.2 g of Li^+TCNQ^- in 50 mL of acetonitrile was added to a hot solution of $Me_2Py^+I^-$ in 50 mL of acetonitrile. The volume of the resultant blue acetonitrile solution was reduced to 25 mL by heating, and, upon cooling, a 6% yield of small, green, elongated crystals was obtained.

The product is Z-β-(N-methyl-2-pyridyl-α-cyano-4-styryl dicyanomethide (P3CNQ, VII). Elemental analysis: calculated (found) for $C_{18}H_{12}N_4$: C, 76.04% (75.46); H, 4.25 (4.20); N, 19.71 (19.77). The solution spectrum of P3CNQ in acetonitrile does not show the typical $TCNQ^-$ bands, but a new broad peak appears at 592 nm. The remainder of this paper will discuss only the latter product (P3CNQ).

Magnetic Measurements

Static susceptibility measurements were made on a microcrystalline sample using a Faraday balance.

Crystal Structure Determination

An acicular crystal was mounted on an ENRAF-Nonius CAD-4F diffractometer; graphite-monochromatized Mo Kα (λ = 70.926 pm) radiation was used. The crystal was determined to belong to space group $P2_1/c$ with unit cell constants $\underline{a}$ = 1493.5(2) pm, $\underline{b}$ = 720.9(2) pm, (needle axis), $\underline{c}$ = 1380.2(3) pm, β = 107.06(2)° with Z = 4 molecules of formula $C_{18}H_{12}N_4$ per unit cell, unit cell volume V = 1.4206(7) nm^3, calculated density 1.33 Mg m^{-3} and observed density 1.32 Mg m^{-3}. 1917 unique diffracted data with $F_{obs} > \sigma(F_{obs})$ were collected in the bisecting geometry. After MULTAN-78[66] yielded the usual infinite hexagonal bathroom-tile solution, recycling of a chemically significant fragment as having correct angular orientation but unknown position revealed the position of all non-hydrogen atoms. The least-squares refinements converged to the final solution, with atom positions as given in Table 1; the final unweighted agreement residual was R = 5.1 per cent (weighted R_W = 6.1 per cent, with weights w =

Table 1. Final Atomic Positions in the P3CNQ Crystal Structure

Atom	x/a	y/b	z/c
N1	0.5612(2)	0.2189(4)	0.5416(2)
N5	0.6813(1)	0.0535(4)	0.8593(2)
N14	1.1016(2)	0.2964(4)	0.4945(2)
N21	1.3240(1)	0.1407(3)	0.8217(1)
C2	0.6257(2)	0.1872(4)	0.6089(2)
C3	0.7058(2)	0.1492(3)	0.6909(2)
C4	0.6911(2)	0.0964(4)	0.7833(2)
C6	0.7991(2)	0.1621(3)	0.6814(2)
C7	0.8769(2)	0.1252(3)	0.7661(2)
C8	0.9663(2)	0.1290(3)	0.7592(2)
C9	0.9851(1)	0.1689(3)	0.6681(2)
C10	0.9083(2)	0.2132(3)	0.5846(1)
C11	0.8183(2)	0.2081(3)	0.5911(2)
C12	1.0812(1)	0.1682(3)	0.6610(2)
C13	1.0929(2)	0.2383(4)	0.5676(2)
C15	1.1575(1)	0.1179(3)	0.7374(1)
C16	1.2537(1)	0.1064(3)	0.7338(1)
C17	1.2794(2)	0.0555(4)	0.6492(2)
C18	1.3712(2)	0.0379(4)	0.6518(2)
C19	1.4396(2)	0.0743(5)	0.7414(2)
C20	1.4148(2)	0.1239(4)	0.8242(2)
C22	1.3038(2)	0.1914(4)	0.9163(2)
H7	0.865(1)	0.099(3)	0.832(1)
H8	1.018(1)	0.106(3)	0.821(2)
H10	0.919(1)	0.240(3)	0.520(1)
H11	0.769(1)	0.236(3)	0.535(1)
H15	1.145(1)	0.088(3)	0.800(1)
H17	1.230(1)	0.031(3)	0.590(1)
H18	1.390(1)	0.002(3)	0.591(1)
H19	1.501(1)	0.067(3)	0.746(2)
H20	1.458(1)	0.150(3)	0.886(2)
H221	1.363(2)	0.213(4)	0.966(2)
H222	1.261(2)	0.295(3)	0.903(2)
H223	1.272(1)	0.095(3)	0.940(2)

$4/F_o/^2(Lp)^2/[\sigma^2(I_{raw}) + (0.05\ I_{raw})^2])$, and the final estimated error of an observation of unit weight was 1.66 (with 1815 observations used in the refinement, and 247 parameters, including positions and anisotropic temperature factor for the C and N atoms, and positions and isotropic temperature factors for the H atoms).

The computer programs MULTAN-78[66] and ORTEP[67] were run on DEC 1077 and IBM 4341 computers respectively, all other crystallographic programs were part of the SDP[68] program package on a PDP-1134 minicomputer.

Charge Distribution and Lattice Energies

INDO[69] atom-in molecule partial charges q_i and the molecular dipole moment were determined using program CNINDO.[70] The Madelung, London, dispersion and ad hoc repulsion lattice energies (the first using the q_i, the latter two using structure-independent parameters of Williams[71] and Govers[72], but without C-H bond foreshortening) were computed using program CELMAP and EWALD.[73,74] All three programs were run on the DEC 1077 computer.

RESULTS

Magnetic Properties

The static magnetic susceptibility measurements on P3CNQ show it to be diamagnetic, with a molar susceptibility in close agreement with the value predicted using Pascal's constants.

Crystal and Molecular Structure

The molecular geometry of P3CNQ is shown in Fig. 2. The atom thermal vibration ellipsoids are drawn by ORTEP[67] at the 50 per cent probability level. Chemically significant bond distances (in pm) and bond angles (degrees) are given. The standard deviations of bond lengths not involving hydrogen atoms are ± 0.2 pm, except where indicated. The bond lengths within the tricyanoquinodimethan portion of the molecule and within the pyridinium ring are benzenoid

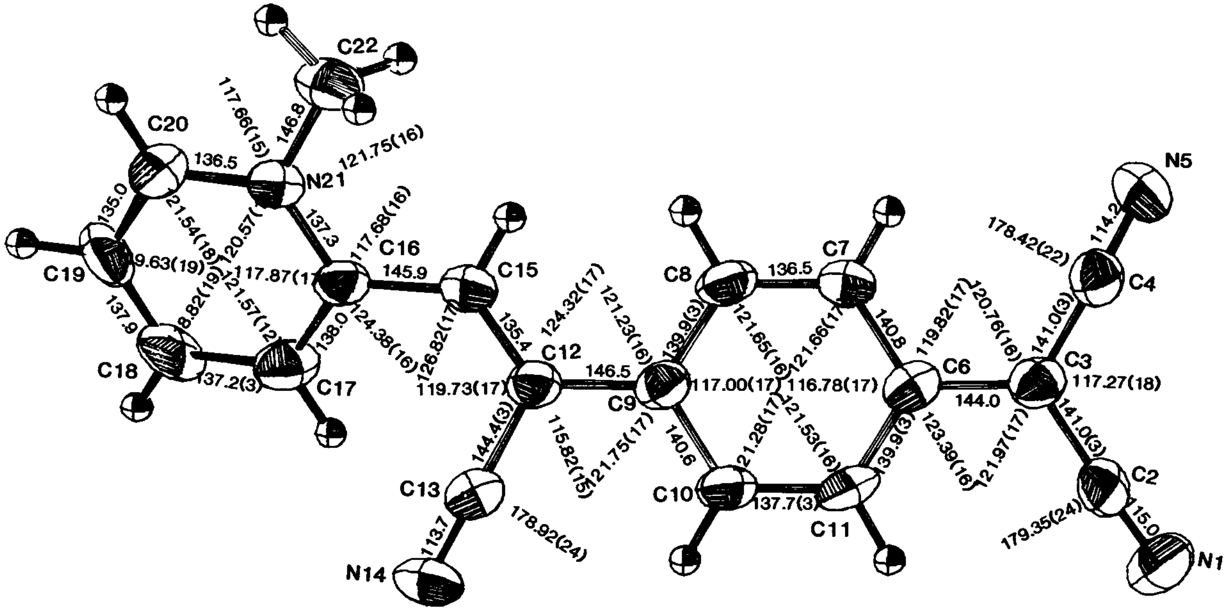

FIGURE 2. ORTEP plot of picolyltricyanoquinodimethan

rather than quinonoid; there is clearly a double bond between C12 and C15. The least-squares plane of the pyridinium ring is twisted 30.13° from the least-squares six-membered ring of the quinodimethan.

The molecules stack along the crystallographic b axis; the intermolecular overlap (the quinodimethan least-squares planes are 354 pm apart) is shown in Fig. 3: the overlap clearly gives zero net dipole moment for the two P3CNQ nearest neighbors, and achieves $D^+ A^-$ stacking along b. The packing of the four P3CNQ molecules in the unit cell is shown in Fig. 4: one can see the orientation of the two chains stacked along b, but mutually related by the glide plane symmetry operator of space group $P2_1/c$.

Atom-in-molecule Charges

The INDO atom-in-molecule charges are shown in Fig. 5: the charges on N1, N5 are typical of cyano N atoms for the $TCNQ^-$ anion; the charge on N14 is typical of a cyano N atom in neutral TCNQ. The charge distribution within the pyridinium ring does not put the bulk of the positive charge on N21 (as would be expected by naive valence bond theory), but rather distributes it throughout the pyridinium ring and the bridge bonds. The computed INDO dipole moment, 26.16 Debyes (8.726×10^{-26} C m) is very large and typical of a zwitterion.

Lattice Energies

The Madelung, London dispersion (=van der Waals) and repulsion lattice energies (E_m, E_d, and E_r respectively) were computed. The computed values are $E_m = -70.434$ kJ/mol (-0.729824 eV), $E_d = -265.903$ kJ/mol (-2.755854 eV), $E_r =$ 133.323 kJ/mol (1.381774 eV), therefore $E_m + E_d + E_r =$

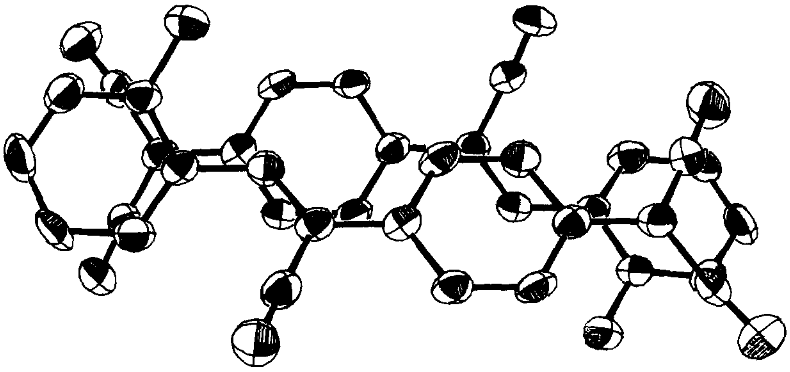

FIGURE 3. Overlap of two P3CNQ molecules stacked along the b axis.

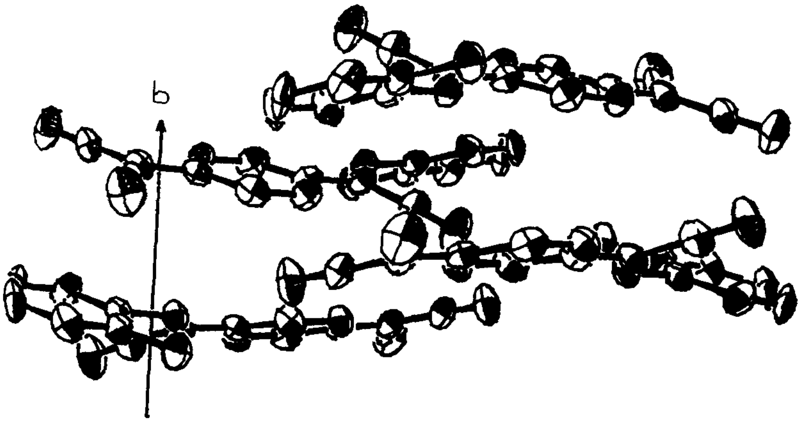

FIGURE 4. Plot of unit cell of P3CNQ, showing two stacks related by the glide plane symmetry operator.

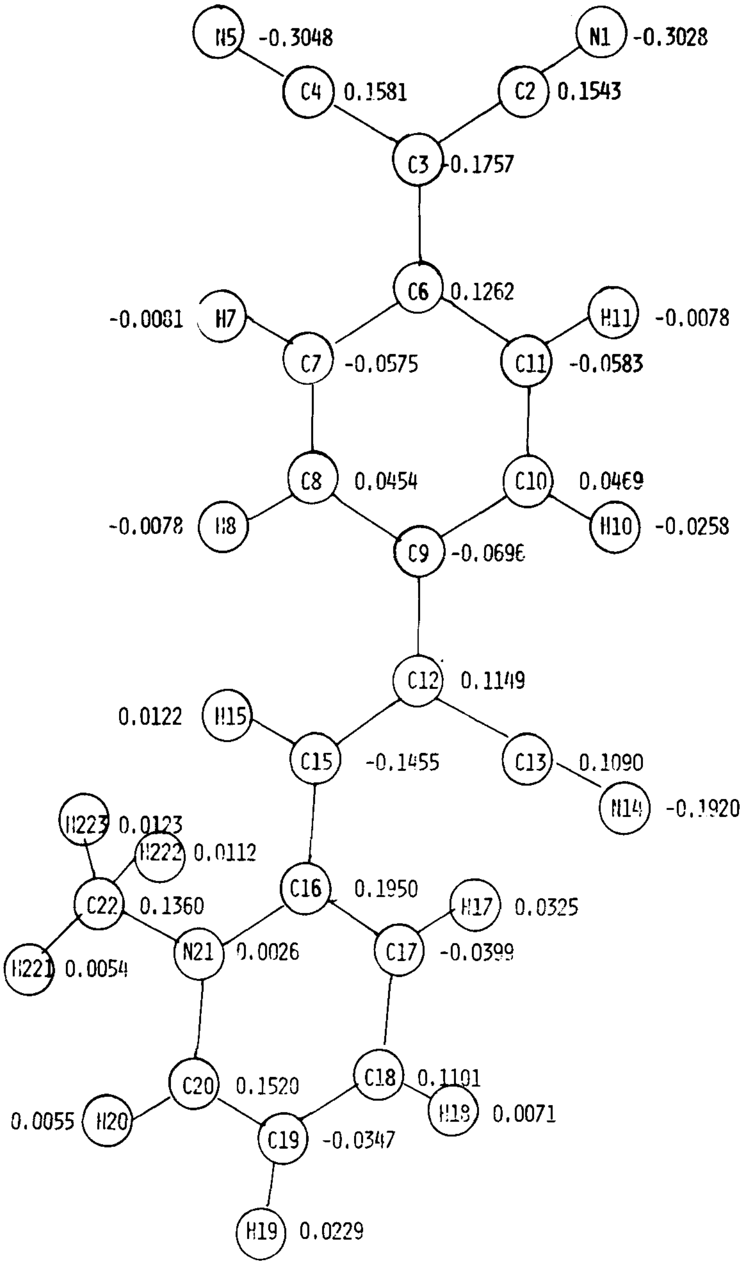

FIGURE 5. INDO charges for P3CNQ.

−203.014 kJ/mol (−2.103904 eV).

DISCUSSION

The chemical analysis and the solved crystal structure indicate that the following reaction occured:

$$\tfrac{1}{4}O_2(CH_3CN) + C_7H_{10}^{+}I^{-}\ (CH_3CN) + Li^{+}C_{12}H_4N_4^{-}\ (CH_3CN) \dashrightarrow$$
$$C_{18}H_{12}N_4(\text{crystal}) + Li^{+}I^{-}(CH_3CN) + HCN + \tfrac{1}{2}H_2O$$

where dissolved O_2 is the presumed oxidizing agent.

The crystal packing, molecular structure, diamagnetism, and INDO dipole moment confirm that P3CNQ is a diamagnetic zwitterionic molecule.

If one sums the partial charges of N1, C2, C3, C4, N5 (−0.4709) and those of C16, C17, C18, C19, C29, N21 and associated H atoms (0.6180), the zwitterionic charge separation becomes quite clear. While measurements of the experimental dipole moment of P3CNQ are in progress, one may compare its calculated INDO dipole moment (26.16 D) and distance d(C3-N21) = 887.1 pm with the corresponding data for p-tricyanovinyldimethylaniline (TCVDMA, Fig.1,VIII) [experimental dipole moment 10.9 ± 0.9 D in benzene,[28,38] distance d(C3-N1) = 659.8 pm[31]]: the charge separation in P3CNQ is clearly more dramatic.

The Madelung energy is smaller than for ionic mixed simple regular salts[75] (e.g. $TMPD^{+}TCNQ^{-}$) whose $D^{+}A\ D^{+}A^{-}$ stacking is approximated in P3CNQ along the b axis. However, the tilt in the pyridinium ring causes the stacking along the b axis to be rather more loose than in typical ionic salts.

The sum $E_m + E_d + E_r$ for P3CNQ is about half the corresponding values for TMPD TCNQ[75] or TTF TCNQ,[76] but is very close to the experimental neutral cohesive energies

U^N_{exp} for anthracene TCNQ,[75] naphthalene TCNQ,[75] TMPD TCNQ,[75] and TTF TCNQ.[76] The problem is that U^N_{exp} is the energy difference between neutral gaseous donors and acceptors and the DA (or D^+A^-) crystal, whereas for P3CNQ the reference gaseous species for E_m is the zwitterion.

A study of how the INDO molecular orbitals of $TCNQ^-$ and pyridinium ion are scrambled by intramolecular electron transfer in P3CNQ is in progress. A more detailed report on P3CNQ is planned.

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