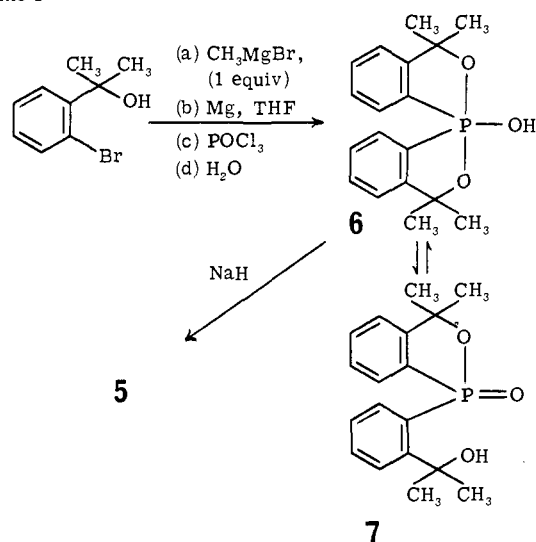


Table II. ^{31}P NMR of **6** (0.026 M in CH_3OH) with Added Sodium Methoxide

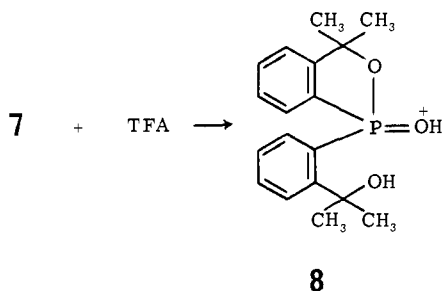
NaOCH_3 , M	$\delta_{31\text{P}}$, ppm	Line width, Hz
0	+51.0	220
0.006	+32.0	55
0.027	+12.5	35
0.046	0.0	30
0.074	-15.1	16
0.126	-22.2	7

Scheme I

solution as the temperature is decreased from $+5$ to -50 $^\circ\text{C}$.

More basic solvents, such as pyridine, increase the relative amounts of **6** in the equilibrium mixture as evidenced by the upfield chemical shift (-12.4 ppm) of the single peak seen at 28 $^\circ\text{C}$ relative to that seen at the same temperature in less basic solvents such as CDCl_3 ($+45.6$ ppm). The further downfield shift ($+81.9$ ppm) and sharpening of this peak upon addition of one part of trifluoroacetic acid (TFA) to nine parts of the CDCl_3 solution is interpreted in terms of protonation of **7**.

Most interesting is the effect of incremental addition of sodium methoxide to a methanol solution (Table II) of **6** or **7**. Progressive sharpening and shift of the ^{31}P NMR signals to higher field are observed, reflecting the formation of **5**.



Moreover, upon addition of excess sodium hydride to THF solution of **6** (or **7**), immediate evolution of hydrogen is realized. Filtration and removal of solvent gives analytically pure sodium salt of **5**.¹⁰ A THF solution of **5** shows a single sharp peak in its ^{31}P NMR at -26.9 ppm.

The similarity in ^{31}P chemical shifts seen (Table II) for solutions of **6** in $\text{CH}_3\text{OH}-\text{CH}_3\text{ONa}$ (as negative as -22.2 ppm) and for the sodium derivative of **5** (-26.9 ppm) or the magnesium derivative of **5** (-20.8 ppm) in THF suggests that sodium methoxide is sufficiently basic to convert **6** to its conjugate base **5**. The detailed dependence of ^{31}P chemical shift on methoxide ion concentration revealed in the data of Table

II suggests that **6** titrates as a weak acid in methanol. In particular one should note that the addition of 1 equiv of base does not produce the chemical shift characteristic of the phosphoroxide anion **5**. Further work will be directed toward a more quantitative assessment of the acidity of **6**.

Acknowledgment. This research was supported in part by a grant to J.C.M. from the National Cancer Institute (HEW PHS CA 13963).

References and Notes

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- (8) Elemental analyses of new compounds are within 0.4% of calculated values. Chemical shifts for ^{31}P are given in parts per million downfield from 85% H_3PO_4 and H chemical shifts are in parts per million downfield from Me_4Si , in CDCl_3 as the solvent, unless otherwise stated.
- (9) Methylmagnesium bromide (1 equiv) was added to THF solution of 2-bromophenyl-2-propanol, followed by magnesium powder (70-80 mesh). The mixture was refluxed for 1.5 h and cooled and POCl_3 (0.48 mol equiv) was added dropwise. The resulting mixture was boiled for 45 min, cooled, and hydrolyzed with aqueous ammonium chloride solution. The usual workup gave **6** (or **7**) in 40% yield: mp 181 $^\circ\text{C}$ (EtOH); ^1H NMR δ 1.74 (6 H, s, Me), 1.79 (6 H, s, Me), 5.90 (1 H, br s, HO), 7.17-7.60 (6 H, m, HAR), 7.94-8.18 (2 H, m, H ortho to P); ^1H NMR (THF- d_6) δ 1.63 (12 H, s, Me), 7.10-7.53 (6 H, m, HAR), 8.03-8.23 (2 H, m, H ortho to P).
- (10) ^1H NMR (THF- d_6) of **5**: δ 1.33 (6 H, s, Me), 1.45 (6 H, s, Me), 6.90-7.31 (6 H, m, HAR), 8.20-8.41 (2 H, m, H ortho to P). The upfield and downfield shifts of the methyls and hydrogen ortho to phosphorus, respectively, as compared with the values for **6** or **7**, are also consistent with the structure shown for **5**.

Itshak Granoth*, J. C. Martin*

Roger Adams Laboratory, University of Illinois
Urbana, Illinois 61801

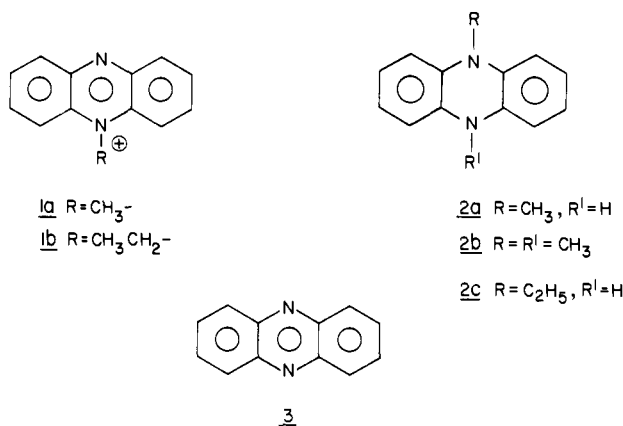
Received April 7, 1978

A Kinetic Model for the Formation of the Conductor *N*-Methylphenazinium Tetracyanoquinodimethanide (NMP-TCNQ)¹

Sir:

Prior to the discovery^{2,3} of the metallic tetrathiafulvalenium tetracyanoquinodimethanide (TTF-TCNQ), the best organic conductor was the 1:1 TCNQ salt of the *N*-methylphenazinium (NMP, **1a**) cation⁴ which exhibits a uniform segregated stack crystal structure.⁵ This 1:1 salt is unusual because at least 28 other 1:1 TCNQ salts of planar closed-shell nitrogen heterocyclic monocations^{4,6-10} are insulators¹¹ with structures that do not exhibit the "infinite chains" of NMP-TCNQ⁵ in the three reported cases.¹²⁻¹⁴ The perspective adopted herein is that the 28 insulating salts constitute "normal" behavior for this subclass of TCNQ salts and that an explanation for the formation of NMP-TCNQ is desirable.

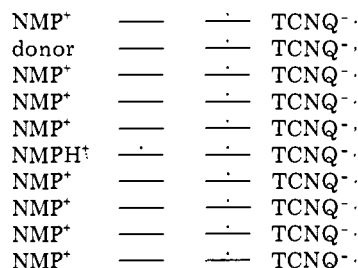
This communication proposes a kinetic model for the formation of NMP-TCNQ involving a donor-acceptor interaction between the acceptor **1a** and any of several donor "impurities" found in precursor salts of **1a** and which persist in NMP-



TCNQ.¹⁵ This is the first order of several models involving specific nonbonded interactions¹⁶ to be proposed for the formation of "unconventional" ion-radical salts such as NMP-TCNQ and TTF-TCNQ.¹⁷ Moreover, the perspective of NMP-TCNQ developed herein has major implications for the low-temperature properties of this phase. While there are several examples¹⁸ where mechanistic pathways have been proposed for chemical transformations, and hence phase formation, in the solid state, the novel aspects of NMP-TCNQ cited afford an opportunity for a phase precipitating from homogeneous solution.

In the course of preparing "high purity" samples of NMP-TCNQ and related materials¹⁹ for conductivity,²⁰ specific heat,²¹ and other physical studies, the isolation of the phase expected from the reaction of methylidihydrophenazine (NMPH, **2a**, and TCNQ²²⁻²⁴) and the isolation of a phase with an x-ray powder pattern consistent with the reported²⁵ $(\text{NMP})_2(\text{TCNQ})_3$ structure concerned the present author. Since many TCNQ salts are handled with no unusual difficulty, the isolation of the TCNQ salt of **2a** suggested that **1a** was reactive under conditions for formation and crystal growth of NMP-TCNQ, a point well precedented.²⁶ In particular, **1a** may be dealkylated to phenazine (**3**) with subsequent carbon methylation of **3**, presumably by a Friedel-Crafts-type mechanism, and is readily reduced to **2a**.²⁶ Hence, one might expect the presence of **2a** and **3**, inter alia,²⁶ in samples of salts of **1a** and NMP-TCNQ. **3** is readily detectable by thin layer chromatography (TLC) in chloroform on silica gel in both NMP-TCNQ and either the methosulfate²⁷ or hexafluorophosphate of **1a**.²⁸ In marked contrast to the salts of **1a**, TLC analysis of the ethosulfate of **1b** (NEP), which forms a 1:1 insulator with TCNQ,⁴ reveals no detectable impurities. Further, when samples of the methosulfates of **1a** or NMP-TCNQ are partially vaporized at 40 °C and 10^{-8} nm in a mass spectrometer, both show peaks at m/e 196 which are more intense than the peak at m/e 195, implying the presence of **2a**.²⁹ Additionally, the methosulfate of **1** exhibits a peak at m/e 208, assignable to a mixture of the constitutional isomers of dimethylphenazine.

The presence of donors **2a**, **3**, and possibly others²⁶ in the presence of the acceptor **1a** suggests a model for the formation of NMP-TCNQ shown in Scheme I, namely a donor-acceptor interaction, facilitated by favorable solution equilibria, between any of the donors present, and **1a**³⁰ initiates formation of a linear cation chain which is then electrostatically compensated by TCNQ anion radicals. Thus, the cation chain in NMP-TCNQ contains variable low levels of **3**, the cation radical of **2a** (**2a**⁺) and possibly their C-methyl derivatives, and the N-methylphenazyl radical,³¹ stabilized in a crystal,¹⁵ ignoring for the present the possible presence of phenazine derivatives arising from reactions of **1a** initiated by visible light or with nucleophiles.²⁶ The presence of the dilute paramagnetic **2a**⁺

Scheme 1^a

^a A simplified representation of NMP-TCNQ. The solid lines represent molecular planes and the dots represent unpaired electrons.

adjacent to a one-dimensional electron gas in NMP-TCNQ invites analogy to the Kondo effect.³²

It is natural to inquire whether the weak donor-acceptor interaction discussed is capable of forming conducting phases with anion radicals other than TCNQ. With 11,11,12,12-tetracyanonaphtho-2,6-quinodimethan (TNAP), it has been reported³³ that **1a** forms both a conducting and an insulating form. With 2,3,5,6-tetrafluoro-TCNQ (TCNQF₄), only an insulating salt with **1a** is reported.³⁴ Both TNAP and TCNQF₄ have reduction potentials higher than that of TCNQ.³⁵

Evidence supportive of the suggestion that "impurities" can cause formation of a conducting phase was obtained by selective³⁶ addition of 15 mol % of the planar **3** and at least 10 mol % of TCNQ, or, conveniently, the TCNQ complex of **3**,¹⁹ to the insulator NEP-TCNQ in acetonitrile solution. The new³⁷ phase which crystallizes contains ~15 mol % of **3**⁶ and has polycrystalline resistivity between 10 and 40 Ω-cm, a decrease in more than nine orders of magnitude compared to NEP-TCNQ.⁴ While the concentration of "impurities" used to form the new phases is significantly larger than in **1a** and the need to add TCNQ suggests the importance of the donor-acceptor pair $\text{TCNQ}^- \cdots \text{TCNQ}$,^{16b} it is clear that specific donor-acceptor interactions in solution have facilitated the conversion of the insulator NEP-TCNQ into a new conducting phase.

The amount of paramagnetic species, such as **2a**⁺ or possibly the N-methylphenazyl radical, presumably randomly distributed in the cation chain, will vary from sample to sample of NMP-TCNQ depending on preparation conditions. Consequently, a significant variation in the magnetic susceptibility of NMP-TCNQ is expected, as reported.³⁸ Moreover, the realization of the presence of random spins in the cation chain has allowed reinterpretation of the origin of the linear term of the specific heat of NMP-TCNQ.²¹

In summary, the phase known as "NMP-TCNQ" does not have a quantitatively³⁹ defined composition, and its formation is qualitatively accounted for by a donor-acceptor interaction involving **1a** and any of several donors present in precursor salts of **1a**.

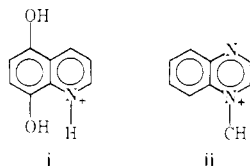
Acknowledgments. The author thanks R. Crandall and F. Elder for the mass spectral data summarized above, G. T. Fekete for the x-ray powder patterns, A. F. Richter for assistance with the synthesis of **2b** and **2c**, and Ann Norton for typing the manuscript.

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- (37) This phase has an x-ray powder pattern distinct from that of NEP-TCNQ, NEP(TCNQ)₂,⁴ and the TCNQ complex of **3**. Anal. Calcd for **1b** TCNQ with 15 mol % of **3**: C, 75.45; H, 3.99; N, 20.66. Found: C, 75.36; H, 3.72; N, 20.80. The unit cell data, collected using Mo K α radiation at Molecular Structure Corporation, is similar to that of NMP-TCNQ.⁵ The crystal is triclinic, space group P1, *a* = 3.817 (3), *b* = 7.920 (25), *c* = 16.181 (18) Å; α = 93.65 (20), β = 94.94 (8), γ = 94.25 (17)°; *V* = 484.8 Å³. Occasionally, preparations of the new phase are contaminated with small amounts of a triclinic prismatic crystal: *a* = 18.561 (10), *b* = 34.222 (19), *c* = 8.117 (2) Å; α = 93.70 (3), β = 94.77 (3), γ = 90.44 (4)°.
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D. J. Sandman

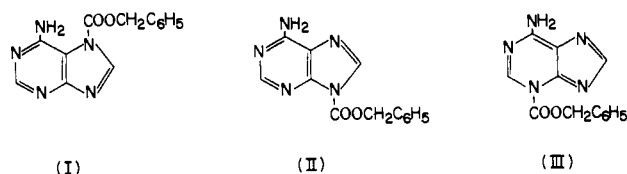
Xerox Webster Research Center, Xerox Square, W114
 Rochester, New York 14644

Received February 1, 1978

Unequivocal Structural Assignments of *N*⁷- and *N*⁹-Acyladenines

Sir:

Reaction products of chloroformates with adenine have been used as intermediates in the synthesis of naturally occurring ureidopurine derivatives.^{1,2} The reaction of adenine with benzyl chloroformate was studied by Altman and Ben-Ishai³ who obtained two products under different conditions, and for which they suggested the structures benzyl 6-aminopurine-7-carboxylate (I) and benzyl 6-aminopurine-9-carboxylate (II) on the basis of their chemical properties and IR and UV spectral data. The former (I) had UV absorption maximum



(λ_{\max} (CH₃CN)) at 291 nm and the latter (II) at 254 nm. These reactions were later reinvestigated by Dyer and co-workers⁴ who concluded that the product II with λ_{\max} at 254 nm is indeed benzyl 6-aminopurine-9-carboxylate (II), whereas the other isomer (λ_{\max} 291 nm) is, in fact, a 3-carboxylate (III) and not a 7-carboxylate (I). Their reassignment of the structure of the second isomer was based on the known occurrence of N-3 to N-9 alkyl migration of 3-alkyladenine derivatives⁵ and on the observation that this compound underwent a facile conversion to the 9-carboxylate. Further, similar to 3-alkyladenines, this compound (λ_{\max} 291 nm) showed a large difference (31 Hz) between the shifts of 2 and 8 protons of the purine ring in the NMR spectrum and a relatively high value for the UV absorption maxima.⁶

Several *N*-acylated purine derivatives have been synthesized in our laboratory,⁷ and we were interested in determining the correct structures of these two reaction products of adenine with benzyl chloroformate for an unequivocal assignment of