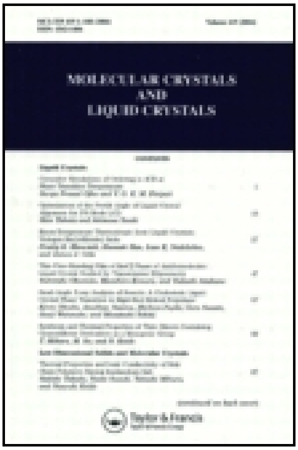


Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

Electrically Conducting Salts of 11, 11, 11 12, 12-Tetracyano-2,6-Naphthoquinodimethane (TNAP)

Gregory R. Johnson [a], Malcolm G. Miles [a] & James D. Wilson [a]

[a] Monsanto Company, St. Lousi, Mo, 63166

To cite this article: Gregory R. Johnson, Malcolm G. Miles & James D. Wilson (1976): Electrically Conducting Salts of 11, 11, 11 12, 12-Tetracyano-2,6-Naphthoquinodimethane (TNAP), Molecular Crystals and Liquid Crystals, 33:1-2, 67-75

To link to this article: http://dx.doi.org/10.1080/15421407608083871

Mol. Cryst. Liq. Cryst., 1976, Vol. 33, pp. 67–75

Printed in Holland

Electrically Conducting Salts of 11,11,12,12-Tetracyano-2,6-Naphthoquinodimethane (TNAP).

GREGORY R. JOHNSON, MALCOLM G. MILES and JAMES D. WILSON
Monsanto Company, St. Lousi, Mo 63166

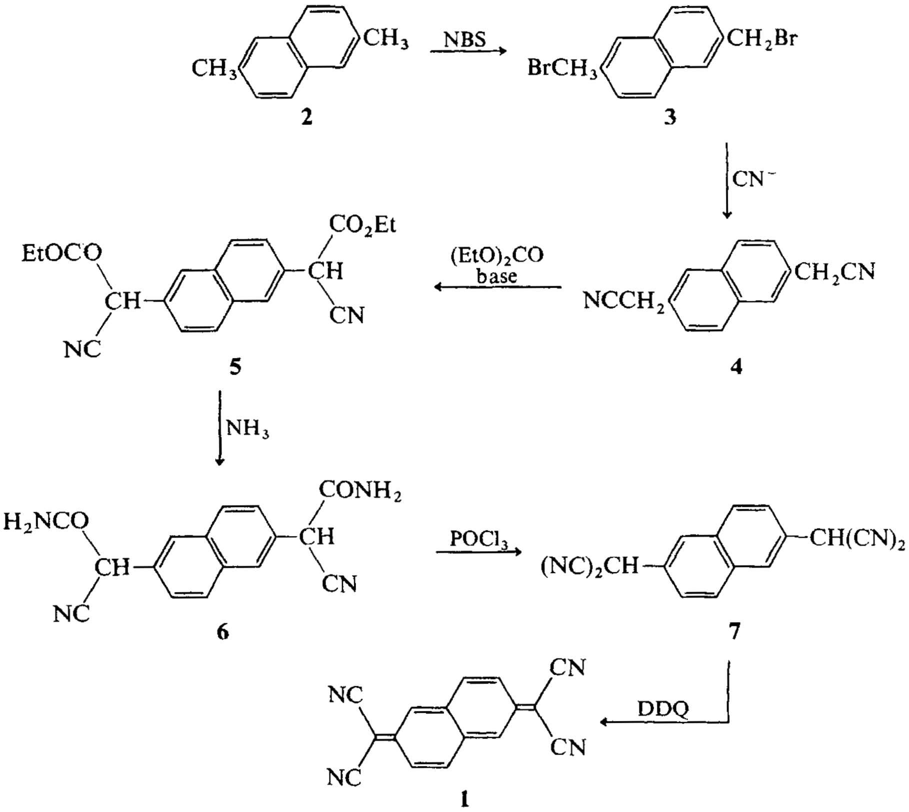
(*Received July 21, 1975*)

The electron-accepting molecule 11,11,12,12-tetracyano-2,6-naphthoquinodimethane (TNAP) forms electrically-conducting solid salts similar in conductivity to those formed by the related TCNQ. Salts of TNAP with both metallic (Na, K, Tl, Cu) and organic (e.g., methyltriphenylphosphonium, N-methylphenazinium) counter-ions were prepared and characterized, and their electrical conductivities measured. The activation energies of $Ph_3MeP(TNAP)_2$ and similar TCNQ salts are related to a structural parameter. The N-methylphenazinium salt was prepared in two allotropic forms. Improvements in the reported TNAP synthesis are described.

The discovery of high conductivity in organic radical ion salts in which both ions are radical species, for example tetrathiafulvalene (TTF) tetracyanoquinodimethane (TCNQ),[1] has initiated an extensive search for other examples of this type of salt. Simple salts of radical anion of 11,11,12,12-tetracyanonaphtho-2,6-quinodimethane (TNAP) were found by Diekmann, Hertler and Benson[2] to have higher conductivities than the analogous TCNQ salts;[3,4] consequently we embarked on a program to explore further the salts of this radical anion.

TNAP Synthesis

A six-step procedure analogous to that developed by Diekmann *et al.*[2] was used (Scheme). Improvements in both the second and final steps allowed the overall yield to be increased from 2% to 12%. The displacement of bromide by cyanide was achieved in 75% yield by treating a suspension of the bromide in DMF at 5°C with a dilute aqueous solution of sodium



cyanide. The yield of the final step was doubled by the simple expedient of adding a dilute solution of 7 in acetonitrile to an excess of the dehydrogenating agent (DDQ). An alternate scheme was recently reported by Sandman and Garito.[5]

Preparation of Salts

Salts of TNAP were prepared by metathesis from one of the lithium, sodium or potassium salts.[2] In this way the following salts were prepared: Tl(TNAP); Cu(TNAP); $Ph_3PMe(TNAP)_2$; (TTT)(TNAP);† and N-methylphenazinium (NMP)(TNAP). As reported by previous workers[2] TNAP and its radical anion are considerably less stable than the TCNQ analogues. The compound shows a strong tendency to polymerise to a pale pink, intractable solid,

---

† (TTT) is the radical cation derived from tetrathiotetracene.

particularly in the presence of a proton source. Thus attempts to prepare salts of triethylammonium, quinolinium and N,N′-diphenyl-*p*-phenylenediamine cations failed to give any of the desired products.

The N-methylphenazinium salt occurs in two allotropic modifications, one pale green-brown and one black. The apparently more stable form was the green modification. This was routinely obtained as the product of metathesis and recrystallization, but occasionally fine black needles were obtained on recrystallization of concentrated solutions in acetonitrile, either as the first crop or mixed with green crystals.

Electrical Properties of TNAP Salts

The conductivity and thermoelectric power of the TNAP salts measured by compaction are given in Table I together with the results reported by Diekmann *et al.*[2] and the results for analogous TCNQ salts. In all cases the TNAP salts have higher or similar conductivities to their TCNQ analogues.

Conductivity measured at room temperatures on five single crystals of $Ph_3PMe(TNAP)_2$ usually fell within the range 0.02–0.04 $ohm^{-1}\ cm^{-1}$, although on several occasions values as high as 0.2 $ohm^{-1}\ cm^{-1}$ were observed. These measurements were made using four electrical contacts

TABLE I

Electrical properties of salts of TNAP and TCNQ

Cation[a]	TNAP			TCNQ		
	$\sigma(ohm^{-1}cm^{-1})$	$S(\mu V\,deg^{-1})$	Ref.	$\sigma(ohm^{-1}cm^{-1})$	$S(\mu V\,deg^{-1})$	Ref.
Na	3.7×10^{-5}		2	3.3×10^{-5}		3
K	1.9×10^{-2}		2	1×10^{-4}	+900	3
	1×10^{-1}	+200		3×10^{-7}	+600	6
Tl	5.3×10^{-2}	+244		4.8×10^{-2}	+406	[g]
Cu	1.3×10^{-1}	−200		1×10^{-2}	−400	3
				5.6×10^{-2}	−365	[g]
Ph_3PMe	1.2×10^{-2}		2	5×10^{-3}	−96	7
	6.2×10^{-2}	−51				
	3.5×10^{-2} [b]			2×10^{-2} [b]		3
				1×10^{-3} [b]		7
NMP	12[c]	−21		2[d]	−24	4, 6
	1×10^{-6} [e]			1×10^{-8} [f]		8
TTT	2.5	−1.4		1.0	−60	[g]

[a] Stoichiometry 1:1 except $Ph_3PMe(TNAP)_2$ and $Ph_2PMe(TCNQ)_2$.
[b] Single crystal.
[c] Black allotrope.
[d] Black allotrope.
[e] Green allotrope.
[f] Purple allotrope.
[g] M. G. Miles and J. D. Wilson, unpublished observations.

of either silver or graphite loaded conducting paint. The current flow was aligned with the long axis of the crystals which was shown by x-ray diffraction to be the TNAP stacking axis.

The temperature dependence of the conductivity was measured from 160 K to 360 K, and is well described by the usual activation formula with a sample dependent E_A ranging from 0.26 to 0.33 eV. (See Figure 1.)

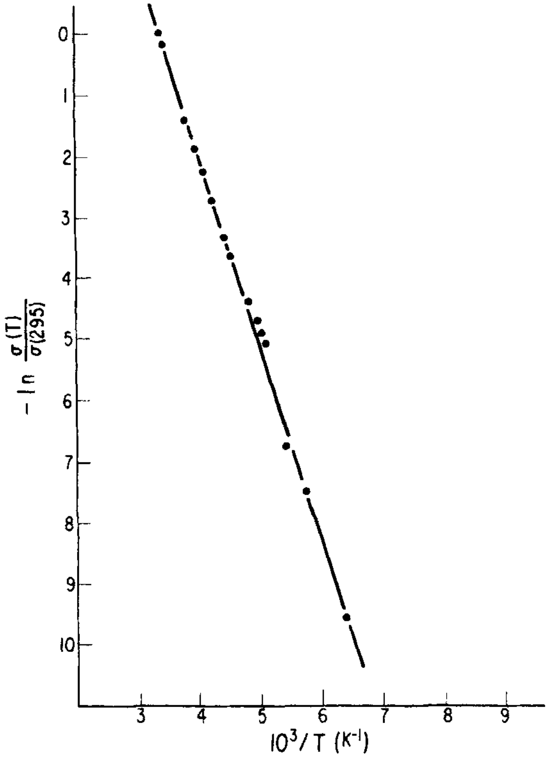


FIGURE 1 Normalized conductivity of $Ph_3PMe(TNAP)_2$ as a function of temperature.

The anomalous values for the conductivity were measured from time to time on the same crystal, and thus cannot be due to different allotropic forms or growth habits. The direct observation of "switching" in one sample gives some clue to the origin of this instability. The resistace of this crystal abruptly rose from 180 Ω to 1200 Ω with negligible change in the activation energy, as measured before and after the event. The two probe (contact) resistances showed little change from 1800 Ω for the voltage leads, but rose from 2400 Ω to 6000 Ω on the current leads. The high and variable contact resistance, together with the unchanging activated behavior suggest that this instability is not an intrinsic property of $Ph_3PMe(TNAP)_2$, but may be due to abrupt changes in the contacts.

Discussion

The compound $Ph_3PMe(TNAP)_2$ crystallizes in a form similar to that reported for the two phases of $Ph_3PMe(TCNQ)_2$ and $Ph_3AsMe(TCNQ)_2$.[9,10,11] The units are triclinic with similar parameters. The radical anions are arranged as homosoric tetrads[10] (with segregated rather than mixed stacking), and these stacks are arranged in sheets separated by the cations. In the case of $Ph_3PMe(TNAP)_2$, the larger radical anion is accommodated by changes in the relation of one sheet with respect to another with little change within sheets. Overlap within tetrads is always of the ring-external bond type with interplanar distance *d*, while overlap at the ends of tetrads is some variety of ring-ring type with interplanar distance *D*. Structural parameters and results of electrical measurements are reproduced for convenience in Table II.†

TABLE II

Parameters for structurally related radical ion salts

Compound	Unit cell parameters[a]		Stacking parameters		E_A
	a b c	α β γ	d D	$\eta = \frac{D-d}{D}$	(eV)
$Ph_3PMe(TNAP)_2$[b]	18.89	117.36	3.30	0.046	0.26–0.33
	14.61	63.42	3.46		
	9.42	111.93			
$Ph_3PMe(TCNQ)_2$[b] (high temperature)	15.78	117.22	3.32 & 3.26	0.064 &	0.33
	14.54	98.05	3.55	0.081	
	8.91	97.02			
$Ph_3PMe(TCNQ)_2$ (low temperature)	15.76	120.01	3.24 & 3.22	0.092 &	0.43
	14.72	97.32	3.57	0.098	
	9.02	96.21			
$Ph_3AsMe(TCNQ)_2$	15.74	120.17	3.20	0.106	0.39
	14.67	96.65	3.58		
	9.01	96.53			

[a] With unit cell as defined in ref. 11b.

[b] $Ph_3PMe(TCNQ)_2$ undergoes a first order phase transition at 315.7°K.

---

† The electrical results tabulated, taken from this work and ref. 8, apply to samples for which the major crystal axes had been identified, and in which the current was applied parallel to the stacking axis.

The measured activation energies of these four compounds seem related to a structure dependent parameter, rather than to the particular moieties involved. Figure 2 shows E_A vs. the alternation parameter η defined by $\eta = (D - d)/D$.

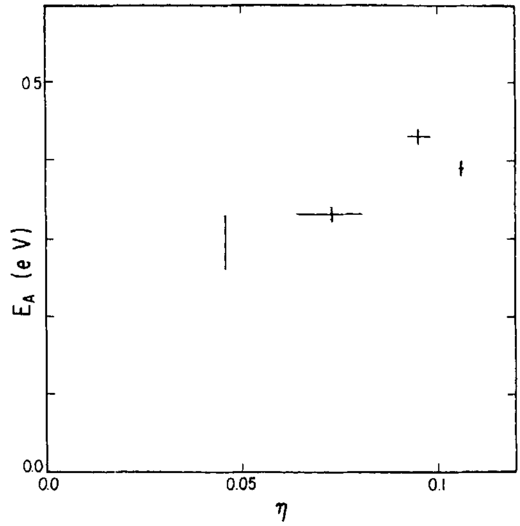


FIGURE 2 Activation energy vs. alternation parameter for structurally related organic semiconductors.

If uniformly spaced, these stacks would be formally described as quarter-filled-band conductors; however, the tetrad arrangement induces a band gap at the Fermi level. The correlation between E_A and η indicates that η is a fair measure of the periodic structural perturbation causing this gap. Such a parameterization is only possible because of the close similarity of these four structures. Room temperature stacking axis conductivities might be expected to depend upon the moieties, but are not compared in detail because of the difficulty in their precise measurement.

In the absence of single-crystal structural and electrical data on the salts of TCNQ and TNAP with cations other than Ph_3XMe, extensive comparisons of the electrical properties of the two classes of salts are unwarranted. This is especially true in the light of the data for the Ph_3XMe salts, which illustrate clearly the effects small and subtle structural changes can have on electrical properties. Nevertheless, the evidence assembled here suggests strongly that, given similar structures, TNAP and TCNQ salts can be expected to exhibit similar solid-state electrical properties.

Experimental

Electrical measurements on compacted microcrystalline samples were obtained by conventional 4-electrode techniques;[12] compactions were pressed at 90,000 psi in a micro pellet press of dimensions 1 × 1 × 5 mm. Silver/pvc paint (duPont Co. #4929) was used to make contact between the probes and the pellet.

2,6-Bis(bromomethyl)naphthalene (**3**), diethyl-2,6-naphthalenedicyanoacetate (**5**), 2,6-naphthalenedicyanoacetamide (**6**), 2,6-naphthalenedimalononitrile (**7**), potassium TNAP, sodium TNAP and methyltriphenylphosphonium $(TNAP)_2$ were prepared after Diekmann *et al.*[2]

2,6-Naphthalenediacetonitrile (4)

A stirred suspension of 2,6-bis(bromomethyl)naphthalene (31.4 g 0.1 m) in dimethylformamide (600 ml) was cooled to 5°C and a cold solution of sodium cyanide (12.5 g, 0.25 m) in water (300 ml) was slowly added. The temperature was kept below 10°C and vigorous stirring was maintained throughout the addition (1 hr). The light tan-colored mixture was allowed to warm up to ambient temperature and then heated to 80°C for 30 mins. Most of the solid present dissolved giving a pale yellow cloudy solution. This was filtered hot and the yellow-orange filtrate was cooled and poured into 3 l of ice water. The white product was filtered off and dried. Recrystallization from acetone containing 10–20% ethanol gave 15.5 g (75%) of the product M.P. 164–166.5° (lit 163.5–165.5).

11,11,12,12-Tetracyano-2,6-naphthoquinodimethane (TNAP, 1)

A solution of 2,6-naphthalenedimalononitrile (5 g, 19.5 mmol) in acetonitrile (1750 ml) under a nitrogen atmosphere was slowly added over 5 hours to a well stirred solution of 2,3-dichloro-5,6-dicyano-1,4-quinone (5 g, 22 mmol) in acetonitrile (150 ml). The product slowly crystallized out of solution as purple plates. After standing overnight 4.1 g (82%) of material was collected.

Thallium (TNAP)

To a solution of thalium acetate (0.15 g, 0.57 mmol) in methanol (20 ml) was added a solution of lithium (TNAP) (0.1 g, 0.38 mmol) in methanol (20 ml). The product immediately precipitated as a black microcrystalline solid. This was collected by filtration, washed with acetonitrile, ether and dried. Yield 0.14 g (82%). Calculated for $C_{16}H_6N_4Tl$: C, 41.71; H, 1.75; N, 12.15%. Found: C, 41.81; H, 1.42; N, 11.95%.

Copper (TNAP)

A solution of lithium (TNAP) (0.1 g, 0.38 mmol) in methanol (30 ml) was treated with a solution of cuprous iodide (75 mg, 0.39 mmol) in acetonitrile (40 ml). Immediate precipitation of a black microcrystalline solid occurred. This was collected by filtration, washed with methanol, acetonitrile and ether and dried. Yield 0.11 g (90%). Calculated for $C_{16}H_6N_4Cu$: C, 60.47; H, 1.90; N, 17.62; Cu, 19.99%. Found: C, 59.11; H, 2.29; N, 17.28; Cu, 20.65%.

N-methylphenazinium (TNAP)

N-methylphenazinium fluorosulfate (0.09 g, 0.30 mmol) was dissolved in acetonitrile (20 ml) and added to a solution of lithium (TNAP) (0.075 g, 0.29 mmol) in methanol (20 ml). A pale green-brown precipitate immediately formed. Yield 0.12 g (93%). This was recrystallized from acetonitrile (200 ml) as pale green highly dendritic crystals with considerable loss due to decomposition. Calculated for $C_{29}H_{17}N_6$: C, 77.49%; H, 3.81; N, 18.70%. Found: C, 76.10; H, 4.00; N, 18.40%. Slow cooling of a saturated solution of NMP(TNAP) occasionally gave 15–20% recovery of black crystals after 3–4 hours. On further standing, crystals of the green-brown allotrope usually developed. Calculated for $C_{29}H_{17}N_6$: C, 77.49; H, 3.81; N, 18.70%. Found: 77.36; H, 3.78; N, 18.97%.

(TTT) (TNAP)

A solution of TTT (0.07 g, 0.2 mmol)[13] in hot 1 : 1 trichlorobenzene/nitrobenzene (25 ml) was added to a solution of TNAP (0.05 g, 0.2 mmol) in dichloromethane (350 ml). Immediate precipitation occurred. The product was filtered off, washed with dichloromethane and ether, and dried. Yield 0.1 g (83%). Calculated for $C_{34}H_{14}N_4S_4$: C, 67.07; H, 2.65; N, 9.19; S, 21.06%. Found: C, 65.36; H, 2.30; N, 8.72; S, 21.08%.

Acknowledgements

The authors are grateful to J. S. Wager for synthetic work, to C. E. Smithey for assistance with electrical measurements, and to D. J. Dahm for useful discussions on the structures.

References

1. J. P. Ferraris, D. O. Cowan, V. Walatka, and J. H. Perlstein, *J. Am. Chem. Soc.*, **95**, 948 (1973); L. B. Coleman, M. J. Cohen, D. J. Sandman, F. G. Yamagishi, A. F. Garito, and A. J. Heeger, *Solid State Commun.*, **12**, 1125 (1973).
2. J. Diekmann, W. R. Hertler, and R. E. Benson, *J. Org. Chem.*, **28**, 2719 (1963).

3a. 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).
3b. W. J. Siemons, P. E. Bierstedt, and R. G. Kepler, *J. Chem. Phys.* **39**, 3523 (1963).
4. L. R. Melby, *Canad. J. Chem.*, **43**, 1448 (1965).
5. D. J. Sandman and A. F. Garito, *J. Org. Chem.*, **39**, 1165 (1974).
6. A. R. Blythe, M. R. Boon, and P. G. Wright, *Discus. Faraday Soc.*, **51**, 110 (1971).
7. Y. Iida, *J. Chem. Phys.*, **59**, 1607 (1973).
8. L. B. Coleman, S. K. Khanna, A. F. Garito, A. J. Heeger, and B. Morosin, *Phys. Letters*, **42A**, 15 (1972).
9. J. Daly and F. Sanz, submitted for publication in *J. Chem. Soc.*
10. D. J. Dahm, P. Horn, G. R. Johnson, M. G. Miles, and J. D. Wilson, *J. Cryst. Mol. Struct.*, **5**, 27 (1975).
11a. A. T. McPhail, G. M. Semeniuk, and D. B. Chestnut, *J. Chem. Soc.* (A), 2174 (1971).
11b. M. Konno and Y. Saito, *Acta Cryst.*, **B29**, 2815 (1973).
12. "Organic Semiconductors," F. Gutmann and L. E. Lyons, ed., John Wiley and Sons, Inc., New York, 1967.
13. C. Marschalk and C. Strumm, *Bull. Soc. Chim. France*, 418 (1948).