

Scheme 2

the corresponding phenol with ^{15}N -nitric acid (95% ^{15}N), gave ^1H n.m.r. spectra consistent with the presence of the ^{15}N label at C-4 {(300 MHz, CDCl_3) δ 1.86 [d, $J(\text{Me}, ^{15}\text{N})$ 3.4 Hz, 4-Me] and 1.94 [d, $J(\text{Me}, 5\text{-H})$ 1.5 Hz, 6-Me]}. Reaction of

the ^{15}N -labelled 4-nitrodienone (1) with nitrogen dioxide in benzene for 2 h (*cf.* ref. 1) gave the C-4-epimeric trinitro ketones (2) and (3), which were separated and their ^1H n.m.r. spectra examined: trinitro ketone (2), ^1H n.m.r. (300 MHz, CDCl_3) δ 1.26 (Bu^t), 1.95 (s, 6-Me), 1.95 [d, $J(\text{Me}, ^{15}\text{N})$ 3.6 Hz, 6-Me], 2.09 (s, 4-Me), 6.11 (s, 5-H), and 6.74 (s, 3-H); ^{15}N -incorporation estimated from 6-Me signal, $40 \pm 5\%$; trinitro ketone (3), ^1H n.m.r. (300 MHz, CDCl_3) δ 1.25 (Bu^t), 1.94 (s, 4-Me), 1.95 (s, 6-Me), 1.95 [d, $J(\text{Me}, ^{15}\text{N})$ 3.0 Hz, 6-Me], 6.53 (s, 3-H), and 6.97 (s, 5-H); ^{15}N -incorporation estimated from 6-Me signal, $37 \pm 7\%$. The assignment of signals reported above was confirmed by appropriate difference nuclear Overhauser effect (n.O.e.) experiments for unlabelled compound (2); for compound (3) HETCOR experiments led to a reassignment of the signals due to 3- and 5-H (*cf.* ref. 1), and difference n.O.e. experiments allowed the assignment of the methyl resonances.

The results reported above may be interpreted in terms of Scheme 2. This Scheme is analogous to that reported earlier² for substrates lacking substituents at C-2 and C-6. Homolysis of ^{15}N -labelled nitrodienone (1) gives the radical pair in a solvent cage (7). Exchange of ^{15}N -nitrogen dioxide with the excess of unlabelled nitrogen dioxide in the system gives radical pair (9). Recombination in these two radical pairs would give the labelled and unlabelled 6-nitro derivatives (8) and (5) respectively, which then undergo 4,5-addition of nitrogen dioxide to give the products (2) and (3), labelled exclusively at C-6.

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Formation of a Zwitterionic Donor-Acceptor Compound based on *N,N,N',N'*-Tetramethyl-*p*-phenylenediamine and 7,7,8,8-Tetracyanoperfluoro-*p*-quinodimethane

Joel S. Miller and Joseph C. Calabrese

Central Research and Development Department, Experimental Station, E328, E.I. du Pont de Nemours and Co., Inc., Wilmington, DE 19898, USA

The reaction of the donor *N,N,N',N'*-tetramethyl-*p*-phenylenediamine (TMPD) with the acceptor 7,7,8,8-tetracyanoperfluoro-*p*-quinodimethane (TCNQF₄) has led to the isolation of a novel type of zwitterionic donor-acceptor compound whose structure has been determined by X-ray crystallography.

The reaction of donors and acceptors has led to the preparation of a plethora of charge transfer complexes exhibiting a variety of unusual optical,¹ electrical,² and, recently, magnetic properties.³ Frequently a neutral or cationic donor, D, forms a molecular solid with a neutral or anionic acceptor, A, exhibiting either segregated or alternating chains of D and A units. In these as well as other cases the D and A units, except for electron transfer, maintain their molecular integrity. In a few cases D-A complexes with 7,7,8,8-tetracyano-*p*-quinodimethane (TCNQ) possess diamagnetic dimers of

[TCNQ]₂²⁻ possessing an (NC)₂C-C(CN)₂ single bond.⁴ Herein we report an example of a new type chemical reaction between a D and A; namely, formation of a covalent zwitterionic complex (1) of composition TMPD/TCNQF₄ from the reaction of the *N,N,N',N'*-tetramethyl-*p*-phenylenediamine (TMPD) donor and the acceptor 7,7,8,8-tetracyanoperfluoro-*p*-quinodimethane (TCNQF₄).

Reaction of TMPD and TCNQF₄ leads to formation of the purple, microcrystalline charge transfer complex of composition [TMPD]⁺[TCNQF₄]⁻.⁵ Attempted slow growth of

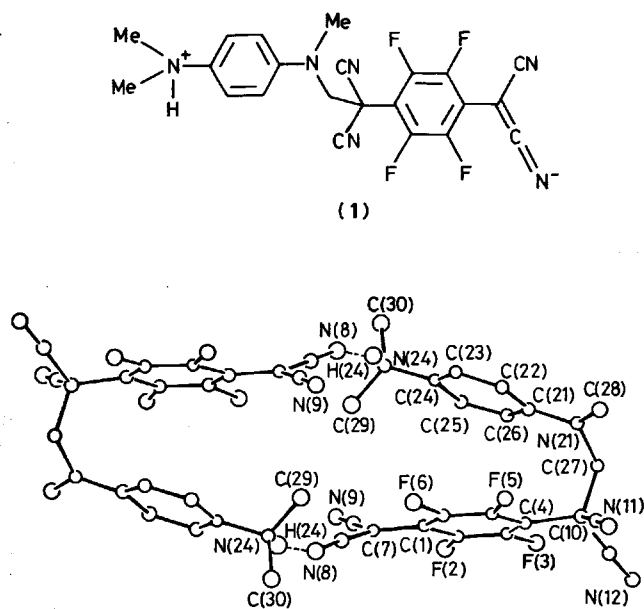


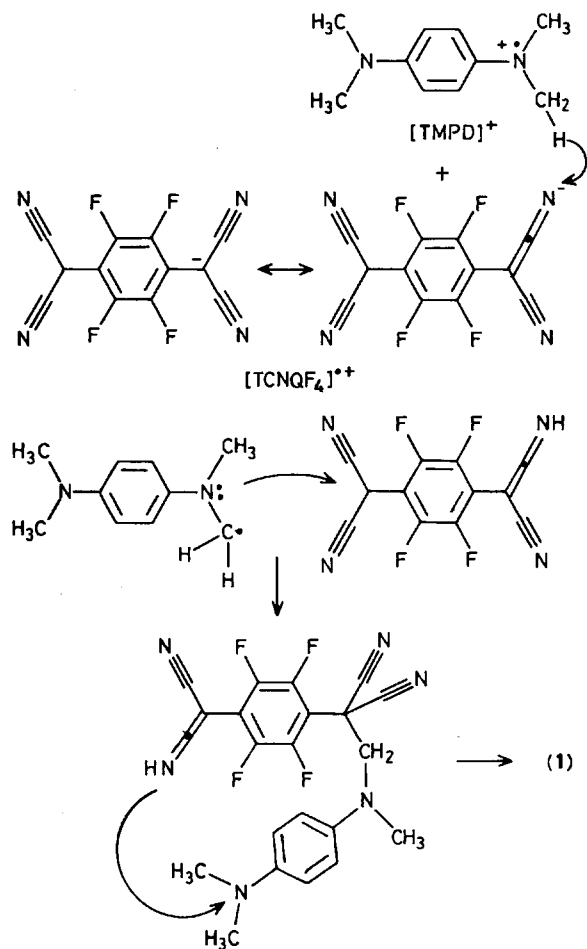
Figure 1. Dimeric structure of (1).

larger crystals suitable for single crystal *X*-ray diffraction study led to the isolation of pale green crystals of (1). The structure (Figure 1)† consists of a dimer comprising a *para*-substituted $-\text{CH}_2\text{N}(\text{Me})\text{C}_6\text{H}_4\text{NMe}_2\text{H}^+$ cationic D moiety bound to an anionic *para*-substituted $-(\text{NC})_2\text{CC}_6\text{F}_4\text{C}(\text{C}\equiv\text{N})(=\text{C}=\text{N})^-$ A moiety *via* an $\text{H}_2\text{C}-\text{C}(\text{CN})_2$ single bond of length 1.591(13) Å. The torsion angle about N(21), C(27), C(10), and C(4) is 63.05° and the distance between the ring centroids is 3.650 Å. The faint green colour of the solid presumably results from a D–A interaction between these adjacent groups in the solid. The molecules form dimers about a centre of symmetry giving rise to unusually short intermolecular N(8) \cdots H(24) and N(8) \cdots N(24) distances of 1.807 and 2.711 Å, respectively. The three N≡C and NC–C distances are 1.138(12), 1.151(12), and 1.155(12) Å and 1.403(14), 1.467(14), and 1.473(14) Å, respectively, whereas the $-\text{N}=\text{C}=\text{C}$ group has shorter and longer bond lengths of 1.174(13) and 1.386(14) Å. This is consistent with the change in hybridization of this bond.

The i.r. spectrum (Nujol) exhibits a broad structured absorption between 2400 and 2700 cm^{-1} assigned to the hydrogen bonded N–H vibration. A pair of intense C≡N absorptions occur at 2156 and 2201 cm^{-1} {*cf.* TCNQF₄, 2228w; [TCNQF₄]^{•-}, 2178s and 2196s, and [TCNQF₄]²⁻, 2133s and 2167s cm^{-1} }.⁶ The $\nu(\text{C}=\text{C}=\text{N}^-)$ vibration is assigned absorptions at 1608 and 1625 cm^{-1} .

A plausible mechanism based upon proton abstraction from alkyl amine radical cations and ketone radical anions⁷ is illustrated in Scheme 1. Without kinetic studies alternative mechanisms, however, cannot be ruled out. The weaker basicity of [TCNQF₄]^{•-} with respect to [R₂CO]^{•-}, however,

† Crystal data: Monoclinic, space group $P2_1/c$; $a = 8.976(1)$, $b = 20.462(6)$, $c = 11.207(2)$ Å, $\beta = 101.91^\circ$, $U = 2014.0$ Å³, $\mu = 1.10$ cm^{-1} , $Z = 4$, $T = -100^\circ\text{C}$. Syntex R3 diffractometer, graphite monochromated Mo- K_α radiation, 3492 data ($4.2^\circ \leq 2\theta \leq 48.0^\circ$), 997 unique reflections with $I \geq 3.0 \sigma(I)$ used in solution (direct methods, MULTAN) and refinement (full-matrix least-squares); isotropic refinement only owing to low data/parameter ratio: $R = 0.069$, $R_w = 0.063$. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.



Scheme 1

suggests that hydrogen radical transfer *via*, for example, a more complex Polonovski-type reaction followed by a Stevens rearrangement may be important.

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