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 (TCNQF$_4$) 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-quino-dimethane (TCNQ) possess diamagnetic dimers of [TCNQ]$_2^{2-}$ possessing an (NC)$_2$C–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/TCNQF$_4$ from the reaction of the N,N,N',N'-tetramethyl-p-phenylene-diamine (TMPD) donor and the acceptor 7,7,8,8-tetra-cyanoperfluoro-p-quinodimethane (TCNQF$_4$).

Reaction of TMPD and TCNQF$_4$ leads to formation of the purple, microcrystalline charge transfer complex of composition [TMPD]$^{\cdot+}$[TCNQF$_4$]$^{\cdot-}$.[5] Attempted slow growth of
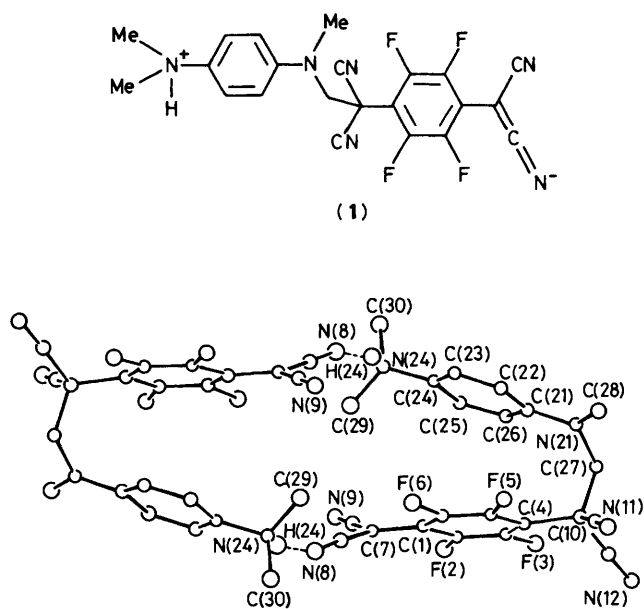
(1)

Figure 1. Dimeric structure of (1).

Scheme 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 $-CH_2N(Me)C_6H_4NMe_2H^+$ cationic D moiety bound to an anionic para-substituted $-(NC)_2CC_6F_4C(C\equiv N)(=C=N)^-$ A moiety via an $H_2C-C(CN)_2$ 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) · · · H(24) and N(8) · · · 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 $^-N=C=C$ 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. TCNQF$_4$, 2228w; [TCNQF$_4$]$^{\cdot-}$, 2178s and 2196s, and [TCNQF$_4$]$^{2-}$, 2133s and 2167s cm^{-1}}.[6] The v(C=C=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 anions[7] is illustrated in Scheme 1. Without kinetic studies alternative mechanisms, however, cannot be ruled out. The weaker basicity of [TCNQF$_4$]$^{\cdot-}$ with respect to [R$_2$CO]$^{\cdot-}$, however,
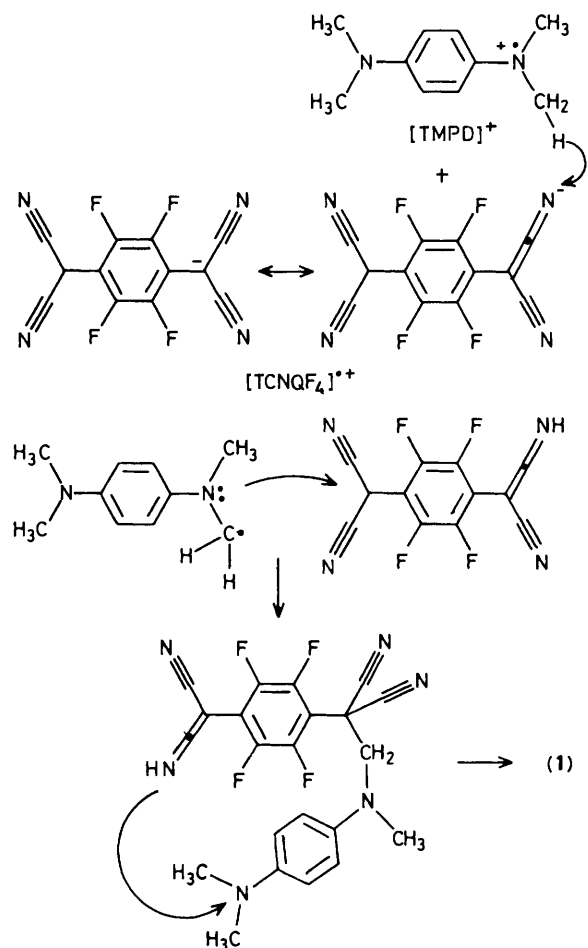
suggests that hydrogen radical transfer via, for example, a more complex Polonovski-type reaction followed by a Stevens rearrangement may be important.

References

1 R. S. Mullikan and W. B. Person, 'Molecular Complexes: A Lecture and Reprint Volume,' Wiley, New York, 1969; Z. G. Soos, Annu. Rev. Phys. Chem., 1974, 25, 121.

2 J. S. Miller, ed. 'Extended Linear Chain Compounds,' vols. 1—3, Plenum, New York; J. Simon and J. J. Andre, 'Molecular Semiconductors,' Springer Verlag, New York, 1985.

3 J. S. Miller, J. C. Calabrese, A. J. Epstein, R. W. Bigelow, J. H. Zhang, and W. M. Reiff, J. Chem. Soc., Chem. Commun., 1986, 1026; J. S. Miller, J. C. Calabrese, H. Rommelmann, S. R. Chittipeddi, R. W. Bigelow, J. H. Zhang, W. M. Reiff, and A. J. Epstein, J. Am. Chem. Soc., 1987, 109, 769; J. S. Miller, A. J. Epstein, and W. M. Reiff, Isr. J. Chem., in the press; G. A. Candela, L. Swarzendruber, J. S. Miller, and M. J. Rice, J. Am. Chem. Soc., 1979, 101, 2755.

4 S. K. Hofmann, P. J. Corvan, P. Singh, C. N. Sethulekshine, R. M. Metzger, and W. E. Hatfield, J. Am. Chem. Soc., 1983, 105, 4608; R. Harms, H. J. Keller, D. Nothe, and M. Werner, Mol. Cryst. Liq. Cryst., 1981, 65, 179.

5 Z. G. Soos, H. J. Keller, K. Ludolf, J. Queckborner, D. Wehe, and S. Flandrois, J. Chem. Phys., 1981, 74, 5287.

6 J. S. Miller and D. A. Dixon, Science, 1987, 235, 871.

7 N. J. Turro, 'Modern Photochemistry,' Benjamin/Cummings, Menlo Park, CA, ch. 10; J. D. Simon and K. S. Peters, J. Am. Chem. Soc., 1981, 103, 6403.

† Crystal data: Monoclinic, space group $P2_1/c$; $a = 8.976(1)$, $b = 20.462(6)$, $c = 11.207(2)$ Å, $\beta = 101.91°$, $U = 2014.0$ Å^3, $\mu = 1.10$ cm^{-1}, $Z = 4$, $T = -100$ °C. Syntex R3 diffractometer, graphite monochromated Mo-K_α radiation, 3492 data $(4.2° \leqslant 2\theta \leqslant 48.0°)$, 997 unique reflections with $I \geqslant 3.0\ \sigma$ (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.