

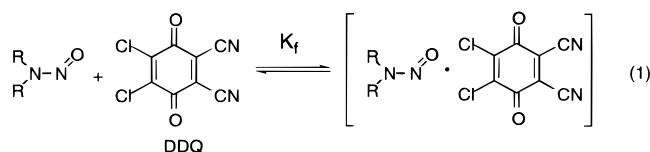
Nitrosamine/2,3-Dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) Complexes and the Formation of Donor-Appended DDQ Chains in the Solid State

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Supramolecular chemistry¹ relies on associative functional group interactions for molecular array formation. In molecular solids, such interactions are the tools of crystal synthesis (or engineering).² As part of a program to uncover *new modes* of organic donor–acceptor (DA) association^{3,4} for application to crystal engineering, we have investigated the DA association of nitrosamines and 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) (eq 1).



The low basicity and high oxidation potential (E_{pox} 1.7–2.2 V vs SCE)⁵ of nitrosamines indicate that they are weak electron donors, and, to the best of our knowledge, no nitrosamine DA complexes have been previously reported, although some metal/nitrosamine adducts are known.⁶ We nonetheless postulated that nitrosamines, as NO n^* donors, might bind to complementary strong π^* acceptors such as DDQ (E_{red} 0.51 V vs SCE). Confirmation of this postulate was afforded by the observance of charge-transfer (CT) absorption bands for nitrosamine/DDQ mixtures. Scheme 1 gives λ_{CT} values and selected K_f data (determined by Benesi–Hildebrand analysis)⁷ for several nitrosamine/DDQ complexes in CH_2Cl_2 .^{8,9} Molar absorptivities for these complexes are $\sim 2000 \text{ M}^{-1} \text{ cm}^{-1}$ near λ_{m} CT. The temperature dependence of K_f for *N*-nitroso-1,1,3,3-tetramethyl-

Scheme 1

Me ₂ NNO	TEMPNO	Ad ₂ NNO
λ_{CT} (nm) 426	494	560
K_f (M ⁻¹)	14.4±1.7	decomposes
iPr ₂ NNO	Nor ₂ NNO	TEMINO
λ_{CT} (nm) 462	490	462
K_f (M ⁻¹)	49.9±5.4	8.8±0.6

isindoline (TEMINO)/DDQ in CH_2Cl_2 yields $\Delta H^\circ -4.8(2) \text{ kcal mol}^{-1}$ and $\Delta S^\circ -11.9(10) \text{ eu}$. The more easily oxidized nitrosamines yield the longer wavelength CT bands as expected.¹⁰

Cooling of red TEMINO/DDQ mixtures in CH_2Cl_2 affords dichoric yellow/red crystals of 1:1 TEMINO/DDQ (**1**) whose structure¹¹ is composed of TEMINO-appended (DDQ)_{*n*} chains (Figure 1), as judged by close intermolecular contacts. Two key interactions are apparent: DA “bonding” of TEMINO to DDQ and carbonyl (C=O⋯C=O) “bonding” between adjacent DDQ molecules.

The 2.87 and 2.67 Å distances of TEMINO N=O atoms to the DDQ carbonyl carbons are much shorter than the atomic van der Waals radii sums (3.22 and 3.25 Å for C⋯O and C⋯N, respectively).¹² The nitrosamine/DDQ complex topology is that expected for an n^* donor/ π^* acceptor complexation. Relevant (AM1-calculated) nitrosamine (Me₂NNO) and DDQ frontier molecular orbitals (FMOs) are shown in Figure 1.

The one-dimensionality of the TEMINO/DDQ array of **1** stems from (DDQ)_{*n*} chain formation via 1,4' C=O⋯C=O association at 2.75 Å.¹³ The topology of this interaction is that of a π nucleophile/ π^* electrophile complex of carbonyl groups.¹⁴ Similar carbonyl bonding is found in the neat DDQ crystal structure **2**,¹⁵ as shown in Figure 2. However, in **2**, the (DDQ)_{*n*} chains¹⁶ have a different (1,1') regiochemistry than that observed

(1) For recent reviews, see: (a) Lehn, J.-M. *Supramolecular Chemistry: Concepts and Perspectives*; VCH: Weinheim, 1995. (b) *The Crystal as a Supramolecular Entity. Perspectives in Supramolecular Chemistry*; Desiraju, G. R., Ed.; Wiley: New York, 1996.

(2) For reviews, see: (a) Desiraju, G. R. *Crystal Engineering: The Design of Organic Solids*; Elsevier: Amsterdam, 1989. (b) Gavezzotti, A. *Acc. Chem. Res.* **1994**, *27*, 309. (c) Reference 1b.

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(5) Sarker, H.; Greer, M. L.; Blackstock, S. C. *J. Org. Chem.* **1996**, *61*, 3177.

(6) (a) Yi, G.-B.; Khan, M. A.; Richter-Addo, G. B. *J. Am. Chem. Soc.* **1995**, *117*, 7850 and references therein. (b) For a bis(nitrosamine)/proton complex, see: Keefer, L. K.; Hrabie, J. A.; Ohannesian, L.; Flippen-Anderson, J. L.; George, C. *J. Am. Chem. Soc.* **1988**, *110*, 3701.

(7) Benesi, H. A.; Hildebrand, J. H. *J. Am. Chem. Soc.* **1949**, *71*, 2703. Our analysis assumes 1:1 DA complexation. A Job plot of λ_{CT} for [TEMINO] + [DDQ] = 0.007 mM in CH_2Cl_2 gives a maximum at [TEMINO] = [DDQ], consistent with preferential 1:1 DA complexation under these conditions.

(8) Nitrosamines were prepared as described in ref 5 except for TEMINO^{9a} which was made by NOCl nitrosation^{9b} of tetramethylisindoline^{9c} in ether/pyridine.

(9) (a) Tönjes, V. H.; Heidenbluth, K.; Scheffler, R. *J. Prakt. Chem.* **1964**, *26*, 218. (b) Back, T. G.; Barton, D. H. R. *J. Chem. Soc., Perkin Trans. 1* **1977**, 924. (c) Griffiths, P. G.; Moad, G.; Rizzardo, E.; Solomon, D. H. *Aust. J. Chem.* **1983**, *36*, 397.

(10) E_{pox} for Me₂NNO, *i*-Pr₂NNO, TEMPNO, TEMINO, Nor₂NNO, and Ad₂NNO are 2.13, 1.91, 1.82, 2.01, 1.87, and 1.45 V vs SCE, respectively, at 200 mV s⁻¹ scan rate in CH_3CN (0.1 M *n*-Bu₄NClO₄) at 25 °C.

(11) X-ray diffraction data on a 0.10 × 0.18 × 0.38 mm red/yellow prism of C₂₀H₁₆Cl₂N₄O₃ (crystal **1**) was collected at 173(2) K using a Siemens SMART diffractometer (Mo K α monochromated radiation, $\lambda = 0.71073 \text{ \AA}$) equipped with a CCD area detector. Crystal **1** gave an orthorhombic unit cell with $a = 9.3590(2)$, $b = 23.4163(3)$, and $c = 9.5319(3) \text{ \AA}$; space group *Pna*2₁, $Z = 4$, cell volume = 2088.95(8) Å³, and $D_{\text{calc}} = 1.371 \text{ g cc}^{-3}$. Data collection (θ 1.74–25.00°) gave 3522 unique observed reflections ($R_{\text{int}} 0.0614$). The structure was solved by direct methods and refined on F^2 with non-hydrogen atoms allowed anisotropic thermal motion. Hydrogen atoms were placed in geometrically calculated positions and allowed to ride on their attached C atoms with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$. Final refinement cycles used 268 parameters and gave R_1/wR_2 ($I > 2\sigma(I$) 0.0588/0.0934, R_1/wR_2 (all data) 0.1085/0.1142, and GOF = 1.151.

(12) All DDQ ring carbons are inside of van der Waals distance of one or the other N=O atoms. van der Waals radii are taken from Bondi, A. *J. Phys. Chem.* **1964**, *68*, 441.

(13) Carbonyl self-complexation has been observed previously for other systems, but its report is rare. For examples, see: (a) Chu, S. S. C.; Jeffrey, G. A.; Sakurai, T. *Acta Crystallogr.* **1962**, *15*, 661. (b) Bolton, W. *Acta Crystallogr.* **1965**, *18*, 5.

(14) For a discussion of carbonyl π Lewis basicity, see: Corcoran, R. C.; Ma, J. *J. Am. Chem. Soc.* **1992**, *114*, 4536.

(15) Zanotti, G.; Bardi, R.; Del Pra, A. *Acta Crystallogr.* **1980**, *B36*, 168. The presence of an intermolecular carbonyl–carbonyl close contact was not mentioned by the authors but is apparent upon analysis of the crystal packing.

(16) In addition, a similar close contact between the carbonyl oxygen and the cyano-substituted ring carbon of DDQ (2.91 Å) is found.

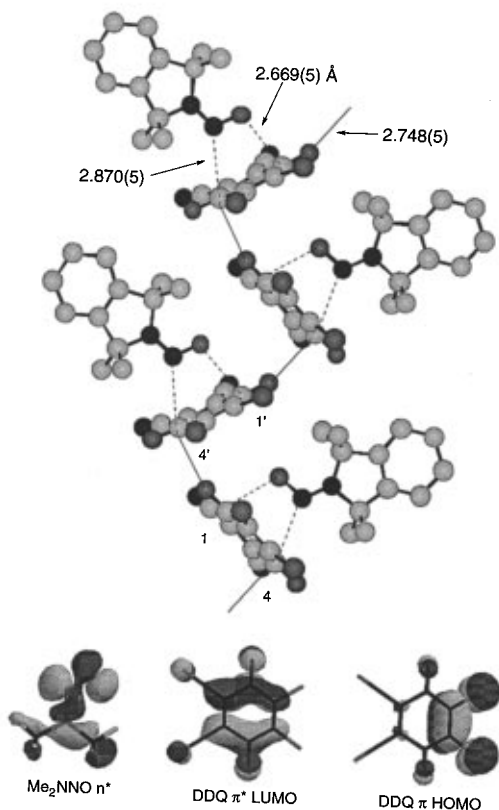


Figure 1. TEMINO/DDQ array of crystal **1** (top) and FMOs of Me₂NNO and DDQ (bottom).

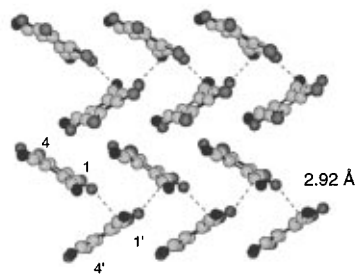


Figure 2. DDQ packing in crystal **2**.

in **1**. We hypothesize that the 1,1' (DDQ)_n regiochemistry in **2** derives from cooperative carbonyl self-association, such that a carbonyl undergoing nucleophilic “attack” becomes a better nucleophile than a carbonyl not under attack; therefore, self-promotion of 1,1' (DDQ)_n chain formation occurs. Accordingly, we postulate that the 1,4' (DDQ)_n regiochemistry in **1** derives from the influence of the TEMINO donor. For a donor-appended DDQ, the two quinone carbonyl groups are presumably electronically (and perhaps sterically) differentiated (so that one is a better Lewis acid and the other a better Lewis base), promoting 1,4' (DDQ)_n formation.

The supramolecular stereochemistry of the (DDQ)_n chains in **1** and **2** deserves mention. In **1** (and apparently also in **2**, although this structure was not solved by us), the DDQ chains are composed of aligned DDQ components to render the strand polar.¹⁷ For convenience, we may visualize the chain dipole

(17) Disorder of the CN and Cl substituents of DDQ, which would render the chain apolar, was looked for in difference density maps and was not apparent.

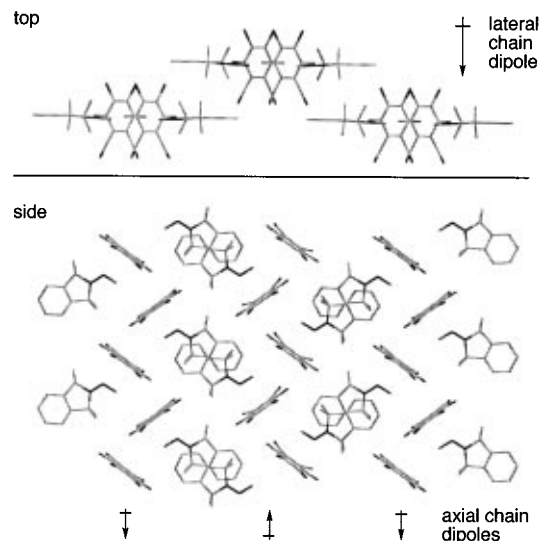


Figure 3. Orthogonal views of packing in TEMINO/DDQ composite crystal **1**.

as the sum of axial and lateral component dipoles. The axial component (which is expected to be small) arises from unidirectional nucleophile–electrophile connectivity along the chain axis, while the lateral dipole component arises from an all-syn intrachain DDQ stereochemistry. The basis for and propensity of such syn stereochemistry is under further investigation. Interchain dipolar orientation determines the bulk polarity of the crystal: crystal **2** is apolar (centrosymmetric) and crystal **1** is polar (noncentrosymmetric). Figure 3 shows the chain packing in crystal **1**, in which axial chain dipoles subtract and lateral chain dipoles add.

In summary, the first DA-bonded nitrosamine/DDQ duplexes and carbonyl-bonded (DDQ)_n chains are reported. The topological specificity of these associative interactions is determined within the TEMINO/DDQ composite crystal **1** and the neat DDQ crystal **2**. The former contains a novel 1D supramolecular array, a donor-appended (DDQ)_n chain, whose regiochemistry appears to be influenced by the nitrosamine donor. The stereochemical preference of syn alignment of DDQ molecules within the DDQ chains of crystals **1** and **2** is noted and, in **1**, culminates in a net polarity of the lattice. Further work to evaluate the theoretical basis of these interactions, their general utility for crystal engineering, and their potential materials value is underway.

Warning! The strong toxicity of the materials used in this work demands that they be handled, stored, and discarded with due respect for the potential hazards involved.¹⁸

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Supporting Information Available: Spectroscopic data for the solution nitrosamine/DDQ complexes and full crystal structure details for **1** (10 pages). See any current masthead page for ordering and Internet access instructions.

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(18) Pruessmann, R.; Stewart, B. W. In *Chemical Carcinogens*, 2nd ed.; Searle, C. E., Ed.; ACS Monograph 182; American Chemical Society: Washington, DC, 1984; pp 643–828.