# Prediction of planarity and reduction potential of derivatives of tetracyanoquinodimethane using *ab initio* molecular orbital theory

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*Ab initio* molecular orbital theory has been shown to account for the distortion from planarity of some derivatives of tetracyanoquinodimethane (TCNQ). The correlation between the reduction potential and the energy of the lowest unoccupied molecular orbital for a set of TCNQ derivatives was used to predict the reduction potential for some novel analogues of TCNQ.

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Tetracyanoquinodimethane[1] (TCNQ, **1**) is widely used as an electron acceptor in charge-transfer complexes and considerable effort has been directed at the design and synthesis of analogues, reflecting interest in the electrical properties of these materials.[2,3] The molecular properties most relevant to the design of novel acceptors are the shape, which determines packing, and the ability to accept an electron, commonly quantified by the reduction potential. While TCNQ is a powerful electron acceptor[2] which has been shown crystallographically to be planar,[4] synthetic elaboration may lead to significant distortion from planarity. For example, steric interactions between cyano and methyl groups force **12** into a non-planar conformation[5] resulting in significant differences between the reduction characteristics of this acceptor and TCNQ.[6]

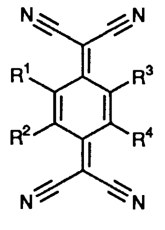
Not surprisingly, the planarity of both donor and acceptor molecules appears to be an important determinant of the conductivity of charge-transfer complexes.[7] This paper will demonstrate that *ab initio* molecular orbital (MO) calculations may be exploited to predict both planarity and the reduction potential of novel TCNQ derivatives.

## Computational details

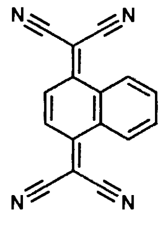
*Ab initio* restricted Hartree–Fock MO calculations were carried out with the SPARTAN electronic structure program.[8] Structures were energy-minimised at the 3-21G(*) level[9] and energies of the LUMOs were calculated at the 6-31G* level[10] using these geometries.† The QUEST3D program was used to extract X-ray crystal structures from the Cambridge crystallographic database.[11] Least squares planes were fitted to the TCNQ substructures of interest using the SYBYL molecular modelling program[12] and the resulting root mean square deviations (RMSD) were used to quantify the planarity of these substructures. The SAS statistical package was used for regression analysis.[13]

## Results and discussion

Planarity is a key issue in the molecular design of electron acceptors for incorporation into charge-transfer complexes. A non-planar molecule will not be able to stack properly and it is unlikely that its electrical properties will be of much interest. To be useful in this area, theoretical methods must first identify those molecules which are planar. The crystal structures for a number of TCNQ derivatives have been determined, providing a necessary test for MO theory.



**1** $R^1 = R^2 = R^3 = R^4 = H$
**2** $R^1 = R^2 = R^3 = H, R^4 = CH_3$
**3** $R^1 = R^2 = R^3 = H, R^4 = F$
**4** $R^1 = R^2 = R^3 = H, R^4 = Cl$
**5** $R^1 = R^2 = R^3 = H, R^4 = CH_3O$
**6** $R^1 = R^4 = H, R^2 = R^3 = CH_3$
**7** $R^1 = R^4 = H, R^2 = R^3 = F$
**8** $R^1 = R^4 = H, R^2 = R^3 = Cl$
**9** $R^1 = R^4 = H, R^2 = R^3 = CH_3O$
**10** $R^1 = R^4 = H, R^2 = R^3 = CN$
**11** $R^1 = R^2 = R^3 = R^4 = F$
**12** $R^1 = R^2 = R^3 = R^4 = CH_3$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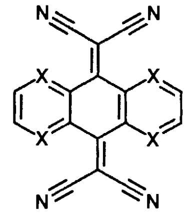
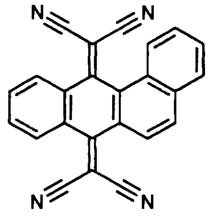


**14** X = CH
**15** X = N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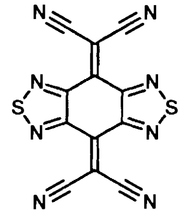

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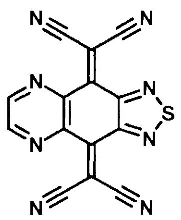

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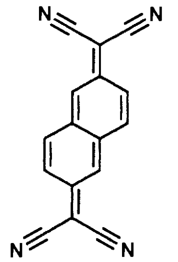
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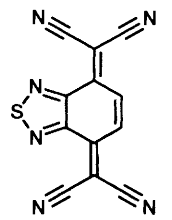

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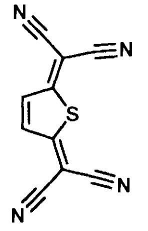

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The approach adopted in this work was to compare crystallographic and calculated geometries for a set of significantly

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† Atomic coordinates for energy-minimised structures and energies calculated at the 3-21G(*) level are available as Supplementary Material which has been deposited under the Supplementary Publications Scheme. For details, see 'Instructions for Authors (1995)', *J. Chem. Soc., Perkin Trans. 2*, 1995, Issue 1 [Supp. Pub. No. 57089, 33 pp.].

non-planar derivatives of TCNQ. The molecular orbital calculations have been carried out at the 3-21G(*) level which is generally accepted as a good compromise between accuracy and computational expense for organic molecules.[14] The heterocyclic analogues **17** and **18** were also included in the analysis because they have been shown experimentally to be planar despite the steric crowding introduced by ring fusion.

The calculated structures are compared with the corresponding crystal structures in Table 1. The calculations agree closely with experiment although they systematically overestimate the distortion from planarity for those structures which are significantly non-planar (RMSD > 3 pm). This may be a consequence of crystal packing forces, but it should also be noted that the uncorrelated wavefunctions used in this study might be expected to exaggerate steric interactions. The heterocyclic derivative, **15**, has also been evaluated; it is predicted to deviate from planarity although to a lesser extent than **14**, in agreement with previously reported semiempirical calculations.[15]

Once a novel TCNQ analogue has been predicted to be planar, its reduction potential becomes relevant. The obvious predictor for this property is the energy, $\varepsilon_L$, of the LUMO and this was calculated at the 6-31G* level for a number of analogues of TCNQ which have either been shown experimentally to be planar or have been predicted to be so (Table 2). Eqn. (1) [where $A = -0.499(0.035)$ V, $B = -4.72(0.23) 10^{-3}$ V mol kJ$^{-1}$, $n = 16$, $r^2 = 0.969$, $F = 436$ and $s = 0.04$ V; standard errors in the parameters have been indicated in parentheses] was fitted to the measured reduction potentials which span 0.67 V and this led to predictions which were all within 0.06 V of the corresponding experimental values.

$$E_1 = A + B\varepsilon_L \qquad (1)$$

**Table 1** Root mean square deviations (RMSD) for the least squares planes fitted to the TCNQ substructures of some analogues of TCNQ

| Structure | Exp./pm[a] | Calc./pm[b] | Refcode[c] |
|---|---|---|---|
| **1** | 0.6 | 0.0 | TCYQME |
| **13** | 52.1 | 56.3 | TCNPQD |
| **14** | 78.8 | 87.7 | DARHUZ01 |
| **12** | 79.7 | 88.0 | CUVLUA |
| **16** | 91.4 | 95.5 | VATHON |
| **17** | 2.6 | 0.0 | FARSOG01 |
| **18** | 2.4 | 0.0 | VOSZAE |
| **15** | — | 18.0 | |

[a] RMSD for crystal structure. [b] RMSD for energy-minimised structure. [c] Refcode for structure in Cambridge crystallographic database.

Having established that $\varepsilon_L$ is a useful predictor of the reduction potential, novel TCNQ analogues for which the energy-minimised structures are planar can be evaluated. This study examines the effects of ring-fusion on TCNQ because this generally leads to inferior electron acceptors and there is considerable interest in extending the π-system of TCNQ without weakening it as an electron acceptor. Predicted reduction potentials for a number of novel, heterocyclic acceptors are presented in Table 3.

Electron acceptors which are similar in shape, but which differ in electron affinity, can be used to probe the relationship between molecular electronic characteristics and the electrical properties of bulk materials. Considerations such as these provided the rationale for the synthesis of the fluorinated TCNQ analogues **3** and **7**.[17,18] The pairs of structures, **22**/**24** and **23**/**25** are particularly relevant in this regard because each pair shows a significant difference in predicted reduction potential while molecular shape remains practically identical.

**Table 3** LUMO energies and predicted reduction potentials for novel TCNQ derivatives

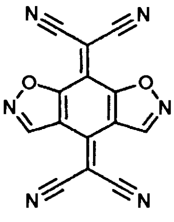
| Structure[a] | $\varepsilon_L$/kJ mol$^{-1}$ [b] | Prd/V[c] | L95/V[d] | U95/V[e] |
|---|---|---|---|---|
| **22** | −195.1 | 0.42 | 0.34 | 0.50 |
| **23** | −186.4 | 0.38 | 0.30 | 0.46 |
| **24** | −94.6 | −0.05 | −0.14 | 0.03 |
| **25** | −85.5 | −0.10 | −0.18 | 0.01 |
| **26** | −158.7 | 0.25 | 0.17 | 0.33 |
| **28** | −156.6 | 0.24 | 0.16 | 0.32 |
| **27** | −146.2 | 0.19 | 0.11 | 0.27 |
| **29** | −144.4 | 0.18 | 0.10 | 0.26 |
| **30** | −166.2 | 0.29 | 0.21 | 0.36 |
| **32** | −147.8 | 0.20 | 0.12 | 0.28 |
| **31** | −226.4 | 0.57 | 0.48 | 0.66 |

[a] RMSD for 3-21G(*) geometries < 1 pm for these structures. [b] Energy of the LUMO from 6-31G* wavefunction and 3-21G(*) geometry. [c] Reduction potential predicted from eq. (1). [d] Lower bound of 95% confidence interval for Prd. [e] Upper bound of 95% confidence interval for Prd.

**Table 2** LUMO energies and reduction potentials for some TCNQ analogues

| Structure[a] | $\varepsilon_L$/kJ mol$^{-1}$ [b] | Exp./V[c] | Prd./V[d] | Res./V[e] | L95/V[f] | U95/V[g] | Refcode[h] | Ref.[i] |
|---|---|---|---|---|---|---|---|---|
| **1** | −146.8 | 0.17 | 0.19 | −0.02 | 0.12 | 0.27 | TCYQME | 2 |
| **2** | −137.9 | 0.17 | 0.15 | 0.02 | 0.07 | 0.23 | | 16 |
| **3** | −165.3 | 0.26 | 0.28 | −0.02 | 0.20 | 0.36 | | 17 |
| **4** | −166.0 | 0.29 | 0.29 | 0.00 | 0.21 | 0.36 | | 2 |
| **5** | −126.6 | 0.07 | 0.10 | −0.03 | 0.02 | 0.18 | | 2 |
| **6** | −129.3 | 0.10 | 0.11 | −0.01 | 0.03 | 0.19 | | 2 |
| **7** | −182.8 | 0.30 | 0.36 | −0.06 | 0.28 | 0.44 | BERZON | 18 |
| **8** | −183.9 | 0.41 | 0.37 | 0.04 | 0.29 | 0.45 | | 2 |
| **9** | −104.9 | −0.01 | 0.00 | −0.01 | −0.09 | 0.08 | | 2 |
| **10** | −231.0 | 0.65 | 0.59 | 0.06 | 0.50 | 0.68 | | 2 |
| **11** | −218.1 | 0.53 | 0.53 | 0.00 | 0.45 | 0.62 | BAKPAE | 2 |
| **17** | −93.7 | −0.02 | −0.06 | 0.04 | −0.14 | 0.03 | FARSOG01 | 19 |
| **18** | −102.5 | −0.01 | −0.02 | 0.01 | −0.10 | 0.07 | VOSZAE | 20 |
| **19** | −160.2 | 0.20 | 0.26 | −0.06 | 0.18 | 0.34 | | 2 |
| **20** | −127.4 | 0.12 | 0.10 | 0.02 | 0.02 | 0.18 | KANWEB | 21 |
| **21** | −108.9 | 0.05 | 0.02 | 0.03 | −0.07 | 0.10 | CYMHTP | 22 |

[a] RMSD for 3-21G(*) geometries < 1 pm for these structures. [b] Energy of the LUMO using 6-31G* wavefunction and 3-21G(*) geometry. [c] Measured reduction potential relative to the standard calomel electrode. [d] Reduction potential predicted by eq. (1). [e] Exp. – Prd. [f] Lower bound of 95% confidence interval for Prd. [g] Upper bound of 95% confidence limit for Prd. [h] Cambridge crystallographic database refcode; RMSD < 3 pm for these structures. [i] Literature references for reduction potential.



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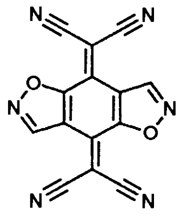

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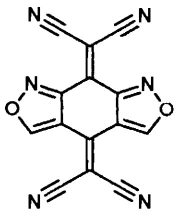

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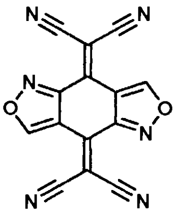

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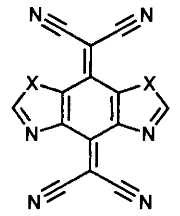
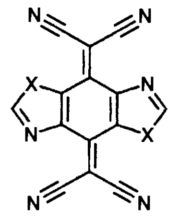
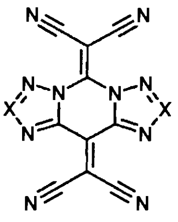


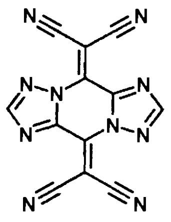
**26** X = O
**27** X = S



**28** X = O
**29** X = S



**30** X = CH
**31** X = C(CN)



**32**

A related group (**26**–**30**, **32**) of heterocyclic analogues, for which the variation in predicted reduction potential was rather less striking, was also examined. These species are all expected to be comparable to TCNQ as electron acceptors, but have the potential to be elaborated synthetically without disrupting the planarity of the TCNQ unit, as exemplified by **31** for which the predicted reduction potential is 0.57 V. Of these structures it is **30** and **32** whose symmetry most closely approximates the $D_{2h}$ symmetry of TCNQ itself.

This work has demonstrated that MO methods can be used to evaluate novel electron acceptors and the results presented suggest that it is possible to extend the π-system of TCNQ without weakening it as an electron acceptor. Some of the molecular frameworks identified by this study could be exploited to provide a conjugated link between two TCNQ units.

## References

1 D. S. Acker and W. R. Hertler, *J. Am. Chem. Soc.*, 1962, **84**, 3370.
2 R. C. Wheland and J. L. Gillson, *J. Am. Chem. Soc.*, 1976, **98**, 3916.
3 L. R. Melby, R. J. Harder, W. R. Hertler, W. Mahler, R. E. Benson and W. E. Mochel, *J. Am. Chem. Soc.*, 1962, **84**, 3374; J. Ferraris, D. O. Cowan, V. V. Walatka and J. H. Perlstein, *J. Am. Chem. Soc.*, 1973, **95**, 948; M. R. Bryce and L. C. Murphy, *Nature*, 1984, **309**, 119; D. O. Cowan and F. M. Wiygul, *Chem. Eng. News.*, 1986, **64**, 2; Proceedings of the International Conference on Science and Technology of Synthetic Metals, 1988, Santa Fe; *Synth. Met.*, 1988/1989, **27–29**; Proceedings of the International Conference on Science and Technology of Synthetic Metals, 1990, Tubingen; *Synth. Met.*, 1991, **41–43**.
4 R. E. Long, R. A. Sparks and K. N. Trueblood, *Acta Crystallogr.*, 1965, **18**, 932.
5 B. Rosenau, C. Krieger and H. A. Staab, *Tetrahedron. Lett.*, 1985, **26**, 2081.
6 A. Kini, M. Mays and D. O. Cowan, *J. Chem. Soc., Chem. Commun.*, 1985, 286.
7 D. O. Cowan, A. Kini, L.-Y. Chiang, K. Lerstrup, D. R. Talham, T. O. Poehler and A. N. Bloch, *Mol. Cryst. Liq. Cryst.*, 1982, **86**, 1; U. Schubert, S. Hünig and A. Aumüller, *Liebigs Ann. Chem.*, 1985, 1216.
8 Version 2.0, Wavefunction Inc., 18401 Von Karman Ave., Suite 210, Irvine, CA 92715, USA.
9 W. J. Pietro, M. M. Francl, W. J. Hehre, D. J. DeFrees, J. A. Pople and J. S. Binkley, *J. Am. Chem. Soc.*, 1982, **104**, 5039.
10 P. C. Harihan and J. A. Pople, *Chem. Phys. Lett.*, 1972, **66**, 217.
11 Cambridge Crystallographic Data Centre, Union Road, Cambridge, CB2 1EZ, UK.
12 Version 6.0, TRIPOS Associates, Inc., 1699 S. Hanley Rd., Suite 303, St. Louis, Missouri 63144-2913, USA.
13 SAS Institute Inc., SAS Circle, Box 800, Cary, NC 27512-800, USA.
14 W. J. Hehre, L. Radom, P. v. R. Schleyer and J. A. Pople, *Ab Initio Molecular Orbital Theory*, Wiley-Interscience, New York, 1986.
15 N. E. Heimer and D. L. Mattern, *J. Am. Chem. Soc.*, 1993, **115**, 2217.
16 J. R. Andersen and O. Jorgensen, *J. Chem. Soc., Perkin Trans 1*, 1979, 3095.
17 J. P. Ferraris and G. Saito, *J. Chem. Soc., Chem. Commun.*, 1978, 992.
18 G. Saito and J. P. Ferraris, *J. Chem. Soc., Chem. Commun.*, 1979, 1027.
19 T. Suzuki, H. Fujii, Y. Yamashita, C. Kabuto, S. Tanaka, M. Harasawa, T. Mukai and T. Miyashi, *J. Am. Chem. Soc.*, 1992, **114**, 3034.
20 Y. Tsubata, T. Suzuki, Y. Yamashita, T. Mukai and T. Miyashi, *Heterocycles*, 1992, **33**, 337.
21 T. Suzuki, Y. Yamashita, C. Kabuto and T. Miyashi, *J. Chem. Soc., Chem. Commun.*, 1989, 1102.
22 N. F. Haley, *J. Chem. Soc., Chem. Commun.*, 1979, 1030.

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