Single Crystal Structure of [(Me₂N-C₆H₄)₂C⁺–⁺C(C₆H₄-NMe₂)₂](I₃⁻)₂: a Twisted Tetraphenylethylene Dication with a C–C Single Bond

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The cyanine distortion of doubly charged ethylenes leading to twisted molecular halves connected by a C–C single bond includes tetrakis(p-dimethylaminophenyl)ethylene, which on twofold oxidation with iodine increases its twist angle ω from 19 to 53° and its central C=C bond length from 135 to 150 pm as predicted by PM3 calculations.

Cyanine perturbations, induced by distributing an even number of electrons over an odd number of centres,[1] inflict some of the most severe structural distortions known: chains with adjacent alternating bonds equalize (A),[1] 'aromatic' π-systems stretch their transannular ring bonds (B)[1,2] or odd-centre zwitterions twist (C).[3]

Cyanine ions can be generated by Lewis or Brønsted acid–base reactions (A and C) or preferentially by redox electron transfer (B) as illustrated here for suitably substituted tetraphenylethylene dianions[1,4] or dications[1,5] including the title compound (Scheme 1).

The solvent-shared contact ion triple of the tetraphenylethylene dianion exhibits a dihedral angle of 56° and a central C–C single bond of length 149 pm[1,4] and the corresponding para-dimethylamino-substituted tetraphenylethylene dication

A, **B**, **C** structural diagrams

[Fig. 1(b)] is twisted by 53° around its 150 pm central C–C bond.

The structural comparison of colourless tetrakis(4-dimethylaminophenyl)ethylene,† prepared by tin reduction of Michler's ketone,[6] and its gold green dication‡ (Fig. 1) reveals as the most noticeable differences the increase in the dihedral angle between the two molecular halves from 19 to 53° and the lengthening of the central C–C bond from 135 to 150 pm. But the removal of two electrons also significantly changes other structural parameters: for instance, the angles C_{ring}–C–C_{ring} widen from 115 to 125° and, above all, the phenyl rings are deformed by a quinoid distortion with a shortening of the bonds C–C_{ring} from 149 to 142 pm, C_{ring}–C_{ring} from 138 to 135 pm and C_{ring}–N from 139 to 133 pm [Fig. 1(b) and (d)]. The dimethylamino groups with angle sums around N of 360° were close to planar already in the neutral molecule.

For further discussion of the structures (Fig. 1), the 'de-phenylated' parent compounds tetrakis(dimethylamino)-ethylene,[7] which owing to its extremely low first ionization potential of only 6.13 eV is oxidized already by pure water,[8] and its dication salts[5] offer additional facets (Scheme 2).

The considerable overcrowdedness caused by the rather bulky dimethylamino groups,[1] enforces an almost 10° increase in the twisting angle between the molecular halves of the neutral molecule, and the cyanine distortion in the dication leads to a 48° change in the dihedral angle and a 16 pm stretching of the central C–C bond.[1,5,7] Other structural changes on two-electron removal are analogous to those in the phenylated derivative (Fig. 1), such as the widening of the central N–C–N angles from 118 to 128° or the shortening of the inner N–C bonds from 140 to 133 pm.[5,7] Altogether, therefore, the twofold oxidation to the
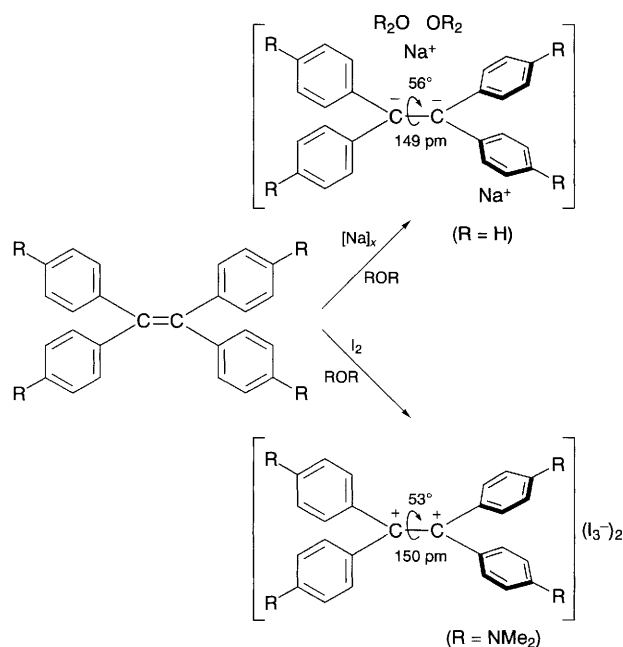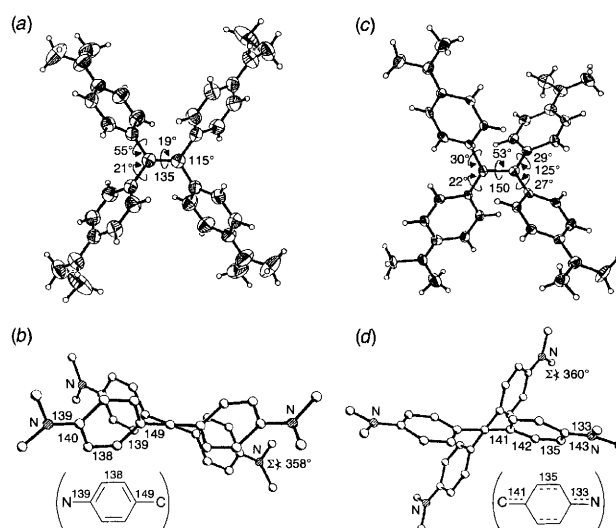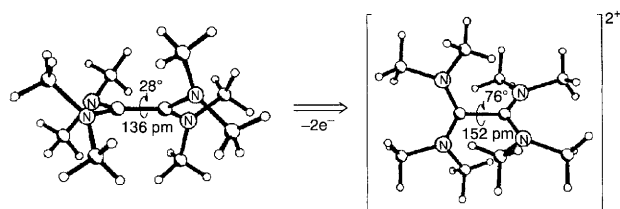

Scheme 1

Fig. 1 Molecular structures of tetrakis(4-dimethylaminophenyl)ethylene: (a) top view with 50% thermal ellipsoids and (b) side view along the central CC axis with essential bond lengths and angles (cf. text; the molecule is located on a crystallographic centre of inversion), as well as of its dication in the bis(triiodine anion) salt (c) top view and (d) side view (cf. text)

Scheme 2
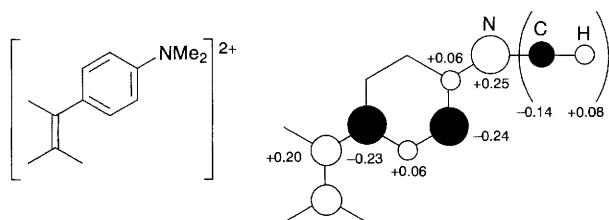
tetraphenylethylene dication (Fig. 1) becomes feasible or is at least greatly facilitated by the four *para*-dimethylamino substituents.

Extensive PM3 calculations§ based on the structural coordinates provide additional information: on optional geometry optimization, the experimental structures are closely approximated and, therefore, represent at least local minima in the $3N - 6 = (3 \times 78) - 6 = 228$ dimensional hyperspace. The difference in the enthalpies of formation, $\Delta\Delta H_f^{\text{PM3}} = \Delta H_f^{\text{PM3}}$ (M^{2+}) $- \Delta H_f^{\text{PM3}}$ (M) $= 2062 - 591 = 1471$ kJ mol^{-1} = 15.2 eV, corresponds to the energy expected for a double ionization to the dication. The charge distribution allows further rationalization of all of the above statements. The two positive charges in the dication are distributed as follows: +0.45 in each of the *para*-NMe$_2$ groups, *i.e.* +1.8 in all four of them and only +0.2 at each C centre of the central C–C bond. Nevertheless, as other known ethylene dications R$_2$C$^+$–$^+$CR$_2$ with substituents R = –NMe$_2$, –C$_3$S$_2$H$_2$ or –C$_6$H$_4$OMe,[5] the one of tetrakis(4-dimethylamino-phenyl)ethylene [Fig. 1(c) and (d)] also exhibits a considerable cyanine distortion (A–C).

The project has been supported by the Adolf Messer Foundation, the Deutsche Forschungsgemeinschaft, the State of Hesse and the Fonds der Chemischen Industrie.

Received, 1st December 1994; Com. 4/07345B

Footnotes

References

1 *Cf.* the review on cyanine distortions in: H. Bock, K. Ruppert, C. Näther, Z. Havlas, H.-F. Herrmann, C. Arad, I. Göbel, A. John, J. Meuret, S. Nick, A. Rauschenbach, W. Seitz, T. Vaupel and B. Solouki, *Angew. Chem.*, 1992, **104**, 564; *Angew. Chem., Int. Ed. Engl.*, 1992, **31**, 550 and references cited therein.

2 H. Bock, A. Rauschenbach, K. Ruppert and Z. Havlas, *Angew. Chem.*, 1991, **103**, 706; *Angew. Chem., Int. Ed. Engl.*, 1991, **30**, 714.

3 W. S. Sheldrick, A. Schönberg, E. Singer and P. Eckert, *Chem. Ber.*, 1980, **113**, 3605.

4 Tetraphenylethylene dianion salt: H. Bock, K. Ruppert and D. Fenske, *Angew. Chem.*, 1989, **101**, 1717; *Angew. Chem., Int. Ed. Engl.*, 1989, **28**, 1685. For other ethylene dianions, see: J. S. Miller, D. A. Dixon, J. C. Calabrese, C. Vazquez, P. J. Krusic, D. Ward, E. Wasserman and R. L. Harlow, *J. Am. Chem. Soc.*, 1990, **112**, 381.

5 Tetrakis(dimethylamino)ethylene dication salts: H. Bock, K. Ruppert, K. Merzweiler, D. Fenske and H. Goesmann, *Angew. Chem.*, 1989, **101**, 1715; *Angew. Chem., Int. Ed. Engl.*, 1989, **28**, 1684; K. Elbl-Weiser, C. Krieger and H. A. Staab, *Angew. Chem.*, 1990, **102**, 183; *Angew. Chem. Int. Ed. Engl.*, 1990, **29**, 211. For other ethylene dications, see: T. Suzuki, H. Shiohara, M. Monobe, T. Sakimura, S. Tanaka, Y. Yamashita and T. Miyashi, *Angew. Chem.*, 1992, **104**, 454; *Angew. Chem., Int. Ed. Engl.*, 1992, **31**, 455, or N. C. Baenziger, R. E. Buckles and T. D. Simpson, *J. Am. Chem. Soc.*, 1967, **89**, 3405.

6 R. Willstätter and M. Goldmann, *Ber. Dtsch. Chem. Ges.*, 1906, **39**, 3775.

7 H. Bock, H. Borrmann, Z. Havlas, H. Oberhammer, K. Ruppert and A. Simon, *Angew. Chem.*, 1991, **103**, 1733; *Angew. Chem., Int. Ed. Engl.*, 1991, **30**, 1678.

8 H. Bock and B. Hierholzer, *Angew. Chem.*, 1988, **100**, 1127; *Angew. Chem., Int. Ed. Engl.*, 1988, **27**, 1069.

9 J. J. P. Stewart, *J. Comput. Chem.*, 1989, **10**, 221.