

Single Crystal Structure of $[(\text{Me}_2\text{N}-\text{C}_6\text{H}_4)_2\text{C}^{+}-\text{C}(\text{C}_6\text{H}_4-\text{NMe}_2)_2](\text{I}_3^-)_2$: 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).

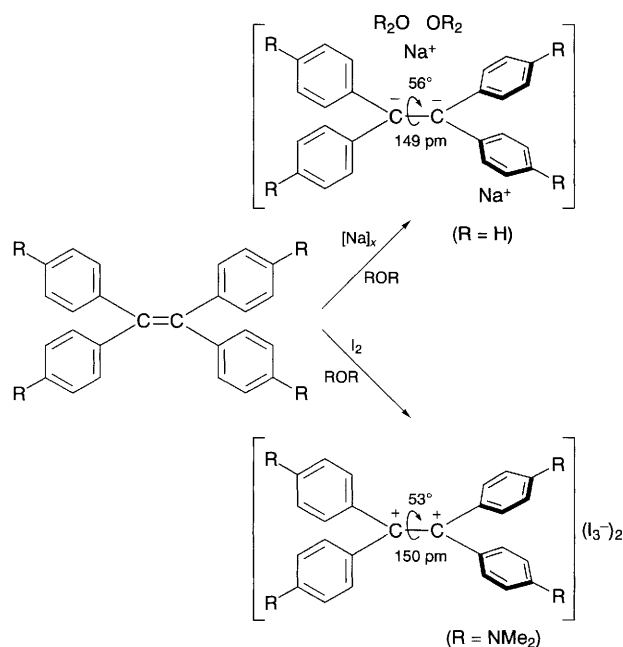
The solvent-shared contact ion triple of the tetraphenylethylene dianion exhibits a dihedral angle of 56° and a central C–C single bond of length 149 pm^{1,4} and the corresponding *para*-dimethylamino-substituted tetraphenylethylene dication

[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 $\text{C}_{\text{ring}}-\text{C}-\text{C}_{\text{ring}}$ widen from 115 to 125° and, above all, the phenyl rings are deformed by a quinoid distortion with a shortening of the bonds $\text{C}-\text{C}_{\text{ring}}$ from 149 to 142 pm, $\text{C}_{\text{ring}}-\text{C}_{\text{ring}}$ from 138 to 135 pm and $\text{C}_{\text{ring}}-\text{N}$ 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 salts⁵ 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

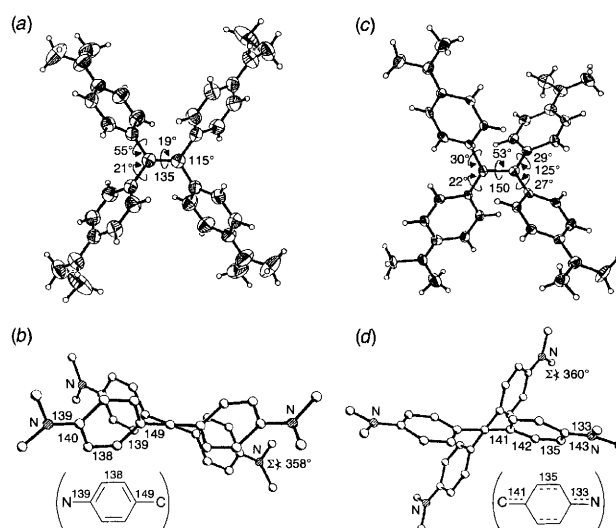
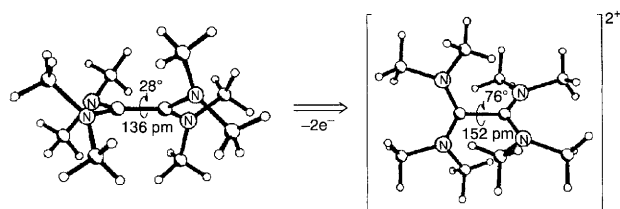
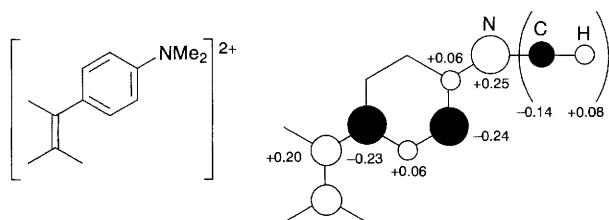


Fig. 1 Molecular structures of tetrakis(4-dimethylaminophenyl)ethylene: (a) top view with 50% thermal ellipsoids and (b) side view along the central CC axis with essential bond lengths and angles (cf. text; the molecule is located on a crystallographic centre of inversion), as well as of its dication in the bis(triiodide 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, $\Delta\Delta H_f^{\text{PM3}} = \Delta H_f^{\text{PM3}}(\text{M}^{2+}) - \Delta H_f^{\text{PM3}}(\text{M}) = 2062 - 591 = 1471 \text{ kJ mol}^{-1} = 15.2 \text{ eV}$, 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*-NMe₂ 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 R₂C⁺-⁺CR₂ with substituents R = -NMe₂, -C₃S₂H₂ or -C₆H₄OMe,⁵ the one of tetrakis(4-dimethylamino-phenyl)ethylene [Fig. 1(c) and (d)] also exhibits a considerable cyanine distortion (A-C).

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Footnotes

† Crystal data: C₃₄H₄₀N₄, M_w = 504.72, a = 2166.6(2), b = 596.1(1), c = 2328.2(2) pm, β = 96.59(1)°, V = 2987.2 × 10⁶ pm³, T = 220 K, ρ_{calc} = 1.122, monoclinic, space group C₂/c (no. 15), Z = 4, Mo-Kα radiation, μ = 0.06 mm⁻¹, STOE-AED-II 4-circle diffractometer, 4503 reflections within 3 ≤ 2θ ≤ 55°, of which 3024 independent and 1989 with I > 2σ(I). Structure solution by direct methods and difference Fourier techniques (SHELXTL PLUS). Refinement with full-matrix least-squares methods

(SHELXTL-PLUS). R = 0.0432, R_w = 0.0497 for 193 parameters and 1989 reflections, R_{int} = 0.0116. W = 1/σ² + 0.00023 F², shift/error < 0.001, extinction correction, residual electron density 0.17/-0.15 e Å⁻³. Heavy atoms were refined anisotropically; hydrogen atoms were geometrically ideally positioned and refined using the riding model with isotropic displacement parameters.

‡ Crystal data: C₃₄H₄₀N₄·2I₃·3CHCl₃, M_w = 1624.28, a = 991.1(1), b = 2824.7(4), c = 1926.4(2) pm, β = 100.56(1)°, V = 5301.4 × 10⁶ pm³, T = 150 K, ρ_{calc} = 2.030, monoclinic, space group P2₁/c (no. 14), Z = 4, Mo-Kα radiation, μ = 3.97 mm⁻¹ (empirical absorption correction). STOE-AED-II 4-circle diffractometer, 12301 reflections within 3° ≤ 2θ ≤ 50°, of which 9121 independent and 5997 with I > 2σ(I). Structure solution by direct methods and difference Fourier techniques (SHELXTL PLUS). Refinement with full-matrix least-squares methods (SHELXTL PLUS). R = 0.0388, R_w = 0.0366 for 535 parameters and 5997 reflections, R_{int} = 0.0312. W = 1/σ² + 0.0002 F², shift/error < 0.001, residual electron density 1.09/-1.09 e Å⁻³. Heavy atoms are refined anisotropically. Hydrogen atoms were geometrically ideally positioned and refined according to the riding model using isotropic displacement parameters. There are three independent anions I₃⁻ in the asymmetric unit, two of them localized around a centre of inversion.

Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

§ PM3 Calculations were performed using our IBM RISC 6000/320 and the program package MOPAC 6.0 (QCPE, Indiana Univ.). Selected geometry optimized structural parameters (pm or °; experimental values in parentheses): M: C=C 135 (135), C_{ring}-C 147 (149), C_{ring}-C-C_{ring} 114 (115). M²⁺: C-C 150 (150), C_{ring}-C 141 (142), C_{ring}-N 137 (134), C_{ring}-C-C_{ring} 127 (125).

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