Tetrahedron Letters, Vol. 34, No. 47, pp. 7553-7556, 1993
Printed in Great Britain

0040-4039/93 $6.00 + .00
Pergamon Press Ltd

STERIC OVERCROWDING IN N-TRIMETHYLSILYL-SUBSTITUTED-P-PHENYLENEDIAMINES: THE ORIGIN OF A WURSTER'S BLUE RADICAL ANION[1,2]

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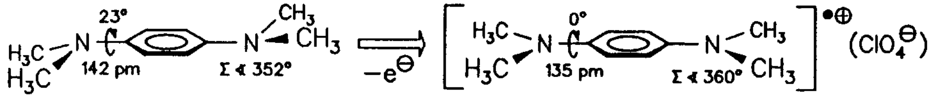
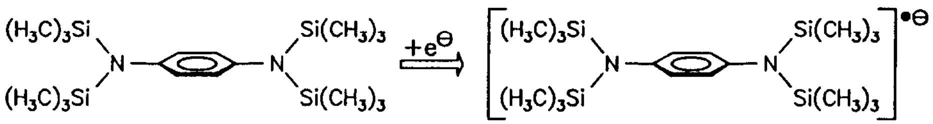
Key words: N-Trimethylsilyl-substituted p-phenylenendiamines, structures

Abstract: The crystal structure of N,N'-bis(trimethylsilyl)-p-phenylene diamine proves an almost planar, though heavily distorted SiHN-C_6H_4-NHSi skeleton, whereas in the sterically overcrowded N,N,N',N'-tetrakis(trimethylsilyl) derivative the p-type electron pairs of the flattened $(R_3Si)_2N$ groups are twisted into the plane of the benzene ring and, therefore, provide a rationale for its unexpectedly possible one-electron reduction to a Wurster's Blue radical anion.

Over a 100 years ago, the dark-blue radical cation salt of N,N,N',N'-tetramethyl-p-phenylenediamine, nowadays named Wurster's Blue, was discovered.[3] Structural comparison of the neutral molecule[4] and its radical cation perchlorate[5] reveals that one-electron oxidation planarizes the molecular skeleton including both $(H_3C)_2N$ pyramids and shortens the NC_{Ring} bonds by 7 pm:[6]



Numerous other neutral or cationic p-phenylenediamine derivatives, stretching from the rather bare parent compound[7] to the sterically shielded monoclinic and triclinic modifications of the tetraisopropyl-substituted one,[8] have been structurally or ESR-spectroscopically characterized. For N,N,N',N'-tetrakistrimethyl(silyl)-p-phenylenediamine, surprisingly, a one-electron reduction to a likewise dark-blue radical anion has been proven by analysis of its ESR signal pattern:[9]



This seemingly strange attempt to reduce an already electron-rich molecule has been stimulated by the assumption that - due to H/H repulsion between the bulky $(H_3C)_3Si$ substituents, exhibiting a van der Waals radius of 380 pm (!),[6] and the adjacent ortho ring hydrogens - the $[(H_3C)_3Si]_2N$ groups should be twisted around the NC_{ring} bond to an extent, which would prevent the electron donating n_N/π-delocalization. Recently,[2] we succeeded in proving the validity of this argument

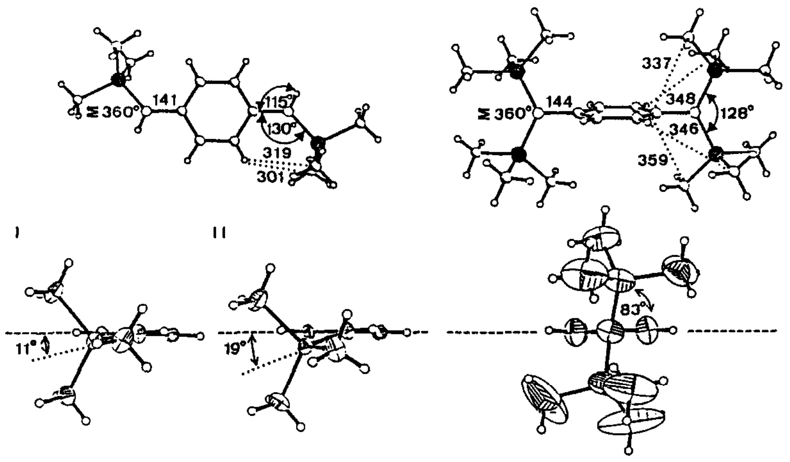


Figure 1. Molecular structures of N,N'-bis(trimethylsilyl)- and of N,N,N',N'-tetrakis(trimethylsilyl)-p-phenylene diamines [10] in side and axial view (50 % thermal ellipsoids)with essential bond lengths as well as distances $\mathrm{C\cdots H_{ortho}}$ (in pm) and angles (in°). Significant differences: dihedral angles $\varpi(\mathrm{SiHN\text{-}C_6}) = 11°$ and 19° for the two independent molecules in the monoclinic unit cell versus $\varpi(\mathrm{Si_2N\text{-}C_6}) = 83°$, bond angles ∢ CNSi = 130° versus ∢ SiNSi = 128° and bond lengths $\mathrm{NC_{ring}}$ = 141 pm versus 144 pm. Cf. text.

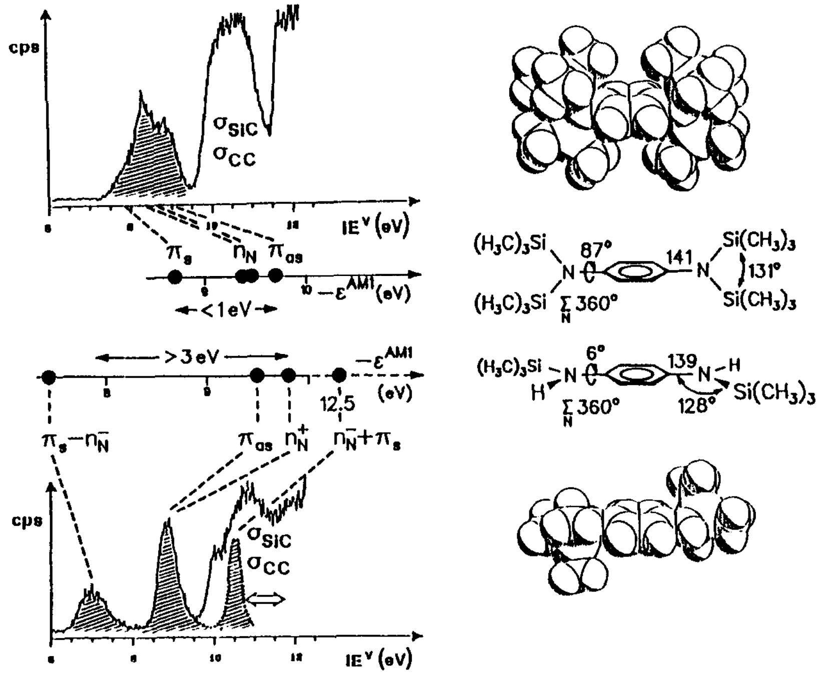


Figure 2. He(I) photoelectron spectra 6 eV - 13 eV of N,N'-bis(trimethylsilyl)- and N,N,N',N'-tetrakis(trimethylsilyl)-p-phenylenediamines[11] with Koopmans' assignment, $\mathrm{IE_n^V = -\varepsilon_J^{AM1}}$ based on eigenvalues of geometry-optimized AM1 calculations and space-filling representations of the resulting structures.[1]

both for the solid by single crystal structure determination[10] (Figure 1) as well as for the gas phase (and accordingly for solution in aprotic solvents) by quantum chemical analysis of the photoelectron-spectroscopic ionization pattern[11] (Figure 2).

The structure-determining influence of the trimethylsilyl groups is clearly visible (Figure 1) In the N,N'-disubstituted p-phenylenediamine, the nitrogen lone pairs of the planar $(R_3Si)HN$ subunits are coaxial with the π-vector perpendicular to the six-membered ring. On the contrary, in the tetrasubstituted derivative, the p-type N electron pairs of the also planar $(R_3Si)_2N$ subunits are twisted into the benzene plane due to the spatial overlap of the bulky $(H_3C)_3Si$ groups with the ortho ring hydrogens and the cancelled n_N/π-delocalization lengthens the NC bond from 141 to 144 pm (Figure 1). As is demonstrated by the existence of both the monoclinic and triclinic polymorphic modifications of the analogous tetraisopropyl-p-phenylenediamine,[8] which exhibit dihedral angles $\varpi(C_2N\text{-}C_6)$ of 28^o and 74^o, respectively, and can be rationalized by energy hypersurface calculations for the rotation of the sterically demanding $((H_3C)_2CH)_2N$ groups around the NC_{ring} bond axes, the interplay of counteracting n_N/π-stabilization and H/H-repulsion determines their structures. This argument can be unanimously extended to the flattened conformations of N,N'-bis(trimethylsilyl)-p-phenylenediamine (Figure 1), in which the overlap between two of the three Si methyl groups and the adjacent ring ortho hydrogen is reduced both by their gauche-arrangement and the astounding widening of the angle CNSi to 130^o(!).

The photoelectron spectra of both compounds (Figure 2), exhibiting n_N/π-ionization bands splits of either smaller than 1 eV or larger than 3 eV, suggest that their gas phase structures as deduced from geometry-optimized AM1 calculations for the assignment of their ionization patterns must approximately resemble the ones in their crystals. Therefore, the sterically congested tetrakis(trimethylsilyl)-p-phenylenediamine should be twisted also in solution and because of both the zero n_N/π-donation and the considerable σ-acceptor perturbation of the benzene ring due to the high effective nuclear charge of the adjacent nitrogen centres, the surprising electron insertion to the 'Wurster's Blue' radical anion is achieved.

Altogether, the molecular ground states of spatially overcrowded organosilicon compounds[12] are subject to sterically enforced structural changes and hindered molecular dynamics. Both change the well-established and often synthesis-applied substituent effects of trimethylsilyl groups. Their further study, therefore, might reveal additional information of general interest.[12]

Acknowledgement. This project has been supported by the Deutsche Forschungsgemeinschaft, the State of Hesse, the Fonds der Chemischen Industrie and the Adolf Messer Foundation. This publication is dedicated to Dr. Johannes Kohl, chairman of the board of directors, Wacker Chemie GmbH, Munich.

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10. Crystal structures: Reflexes are recorded using a four circle diffractometer Siemens AED II with $\lambda(\mathrm{MoK}\alpha) = 0.32\ \mathrm{mm}^{-1}$; structure solution using direct methods and difference Fourier technique (SHELXTL-Plus). **N,N'-Bis(trimethylsilyl)-p-phenylenediamine** $C_{12}H_{24}N_2Si_2$ (252.51), a = 1175.2(2), b = 1219.3(3), c = 1184.3(2) pm, $\beta = 114.40(2)^\circ$, V = 1545.45 x $10^6 \mathrm{pm}^3$ (130 K), Z = 4, $\rho_{\mathrm{calc.}} = 1.085\ \mathrm{g/cm}^3$, monoclinic, space group $P2_1/c$ (Nr. 14 Int. 4104 measured reflexes within $3^\circ < 2\,\Theta < 53^\circ$, of which are 3201 independent and 2702 with $I > 1.5r\ (I)$, $R_{\mathrm{int.}} = 0.0172$, $R = 0.0304$, $R_w = 0.0316$ for 242 parameters, $w = 1/(r^2/F) + 0.00015\ F^2)$, GOOF = 1.860, shift/error < 0.001, extinction correction x = 0.0028(3), rest electron density +0.32/ -0.21 $e_o Å^{-3}$. C, N, Si anisotropically, H isotropically refined. 2 independent molecules within the asymmetric unit. **Tetrakis(trimethylsilyl)-p-phenylenediamine** $C_{18}H_{40}N_2Si_4$ (396.87), a = 653.7(3), b = 835.2(3), c = 1290.6(4), a = 99.83(2), b = 100.14(2), c = $103.05(3)^\circ$, V = 659.21 x $10^6 \mathrm{pm}^3$ (250 K), Z = 1, $\rho_{\mathrm{calc.}} = 0.999\mathrm{g/cm}^3$, triclinic, space group P1 (Nr. 2. Int. Tab.), 3481 measured reflexes within $3^\circ < 2\Theta < 50^\circ$, of which are 2323 independent and 1795 with $I > 2r\ (I)$, $R_{\mathrm{int.}} = 0.0165$, $R = 0.0451$, $R_w = 0.0526$ for 118 parameters, $w = 1/(r^2(F) + 0.00025\ F^2)$, GOOF = 2.679, shift/error < 0.001, extinction correction x = 0.007(2), rest electron density +0.25/ -0.24 $e_o/Å^3$. All C, N, Si atoms are anisotropically refined, H ideally positioned and refined with fixed temperature factors according to the Reiter model. For further structural details cf. the report submitted to the Cambridge Crystallographic Data Centre.
11. He(I)PE spectra are recorded using a LEYBOLD Heraeus UPG instrument at 10^{-4} mbar and 1000 cps, spectra calibration with $^2P_{3/2}$ (Xe/Ar) = 12.13/15.76 eV. AM1 calculations with the SCAMP version 4.1 on a IBM RISC 6000/300.
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(Received in Germany 3 August 1993; accepted 21 September 1993)