Differential Radical Cation Stability from the *cis*- and *trans*-Cyclodiphospha(III)azane Derivatives

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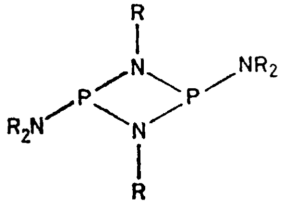
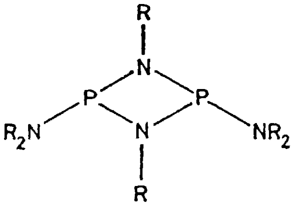
Summary The electrochemical oxidation reactions of *cis*- and *trans*-1,3-di-isopropyl-2,4-bis(di-isopropylamino)-cyclodiphospha(III)azane isomers are quite different; only the trans-(**1**) isomer undergoes a one-electron oxidation reaction to produce a stable radical cation.

WE report the different electrochemical behaviour observed in the oxidation of the isomeric cyclophospha(III)azane derivatives, *cis*-(**1**) and *trans*-(**1**). The preparation, separation, and characterization of these isomers with t-butyl[1a] and with di-isopropylamino groups[1b,2] on the phosphorus

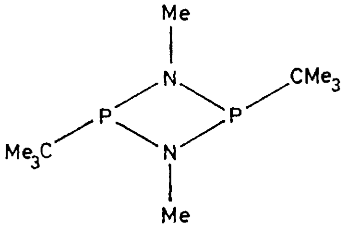


trans—(1)



cis—(1)

R = Pr^i



trans—(2)

atoms have been reported. The isomers have different ring conformations and barrier heights[1c] for rotation about the P–NR$_2$ bond, where the ring is planar in the *trans* isomer and puckered in the *cis*.[3] The n.m.r. spectra of these compounds suggest that these geometric differences are accompanied by significant differences in their electronic structure. Our results show that the oxidation reactions of these electron-rich ring compounds occur at rather low anodic potentials and emphasize the differences in their electronic structure.

The cyclic voltammograms were measured in MeCN containing 0·1 M tetraethylammonium tetrafluoroborate and using a platinum button (0·2 cm^2) working electrode and an aqueous sodium chloride calomel electrode.[4] All measurements were made with *ir* compensation. As may be seen in the Figure, the trans-(**1**) isomer undergoes a one-electron reversible oxidation reaction with $E^{\circ\prime} = 530$ mV to produce an orange coloured cation; $i_{pc}/i_{pa} = 1$ and the peak separation, $|E_{pc} - E_{pa}|$, $= 60$ mV. The i_p values scale linearly with $\nu^{1/2}$ between 20 and 100 mV/s, with $i_p/Ac\nu^{1/2} = 820$ A (V/s)$^{-1/2}$ (mol/cm)$^{-1}$ where A = area in cm^2 and c = concentration in mol cm^{-3}. Thus the reaction is diffusion controlled where the diffusion coefficient is estimated[5] as equal to 9×10^{-6} cm^2/s. Not shown in the voltammogram is the peak for a second oxidation reaction which is irreversible and has E_{pa} at 1600 mV.

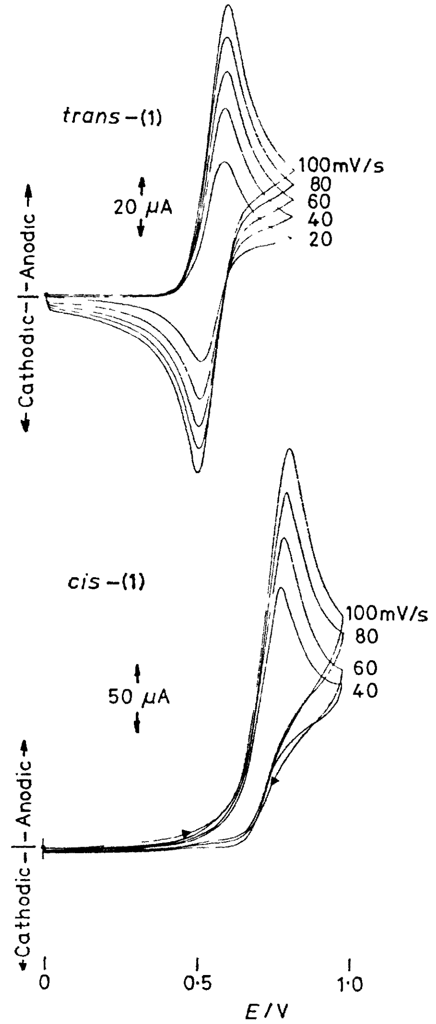


FIGURE. Cyclic voltammogram of *trans*-(**1**) and *cis*-(**1**) in MeCN containing Et$_4$NBF$_4$.

In CH$_2$Cl$_2$ the first oxidation reaction has $E^{\circ\prime} = 550$ mV, indicating that it is not sensitive to solvent changes, although the persistence of the colour near the electrode surface suggests that the cation is more stable in this less nucleophilic solvent. λ_{max} for the cation is *ca.* 430 nm (CH_2Cl_2); however, because we were unable to generate a stable cation solution at room temperature, this measurement could not be made quantitative.

The *cis* isomer of (**1**) is more difficult to oxidize than the *trans* as expected from the photoelectron spectra of analogous compounds.[2] The reaction of *cis*-(**1**) in MeCN is irreversible and produces a peak with E_{pa} at 760 mV. The i_{pa} values scale linearly with $\nu^{1/2}$ indicating a diffusion-controlled reaction; however, the products of this reaction adhere to and alter the electrode surface. A second small peak appears in the voltammogram at 1040 mV.

For comparison, the cyclic voltammogram of the *trans*-di-t-butylcyclophospha(III)azane derivative (**2**) in MeCN shows a very broad wave for an irreversible reaction with E_{pa} at 950 mV.

The cyclophospha(III)azanes are more easily oxidized than a large variety of unsaturated and aromatic compounds. While the oxidation reaction of these compounds is influenced by substituents, the effect is small. For example, the difference in oxidation potential between *p*-diethylbenzene (E_{pa} $+2{\cdot}0$ V[6]) and *p*-dimethylaminobenzene (E_{pa} $+0{\cdot}2$ V[6]) is *ca.* 2 V, while the difference between *trans*-(**1**) and -(**2**) is only 0·4 V. The conformation of the cyclophospha(III)azane ring which is produced by the *cis/trans* arrangement of the substitutions is also an important factor in these reactions. Since the planar *trans*-(**1**) is the only structure which produces a stable radical cation, one can assume that the stabilizing interactions between the non-bonded electron pairs, both in the ring and on the substituents, are best achieved when the ring has a planar conformation. However, it is the combination of the ring planarity and the amino substituents which makes the radical cation stable since both *cis*-(**1**), which is puckered, and the planar (**2**) produce an unstable cation. To the extent that the electronic interaction between the ring and the NR_2 group is also important in the neutral molecule, it may explain why only the trans-(**1**) isomer has a hindered rotation of the NR_2 group at room temperature.[1]

(*Received*, 9*th June* 1980; *Com.* 627.)

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[1] (a) O. J. Scherer and G. Schnabl, *Angew Chem., Int. Ed. Engl.*, 1976, **15**, 772; (b) O. J. Scherer and K. Andres, *Z. Naturforsch., Teil B*, 1978, **33**, 467; (c) contrary to our statement in ref. 1b, *cis*-(**1**) shows no hindered rotation about the P–NR_2 group at room temperature (T_c lies below 20 °C).

[2] R. Keat, A. N. Keith, A. Macphee, K. W. Muir, and D. G. Thompson, *J. Chem. Soc., Chem. Commun.*, 1978, 372.

[3] See, for example S. Pohl, *Z. Naturforsch., Teil B*, 1979, **34**, 256, and references therein.

[4] A. F. Diaz, *J. Org. Chem.*, 1977, **42**, 3949.

[5] R. N. Adams, 'Electrochemistry at Solid Electrodes,' Dekker, New York, 1969.

[6] N. L. Weinberg, 'Technique of Electroorganic Synthesis,' Part II, Vol. V, Wiley, New York, 1975.