mate. Mass spectral analysis showed a strong parent boron envelope with m/e cutoff of 282 (probably $B_{18}H_{20}S_2$); features with lower m/e ratios were not readily apparent due to the fragmentation pattern of this species. The infrared spectrum was similar to $SB_{10}H_{12}$ but not identical. The ^{11}B NMR in benzene appeared to be a 2:1 mixture of $SB_{10}H_{12}$:SB_9H_{11}.

Reduction of 1-SB_9H_9 by Sodium Naphthalide. Dry THF was added to a flask as described above for the other reductions. The system was back-filled with nitrogen, warmed to 25°, and 47.7 mg (2.08 mmol) of Na and 265.8 mg (2.08 mmol) of naphthalene were added. Stirring was continued for 5 h during which time the deep-green sodium naphthalide was generated. Then 143.6 mg (1.04 mmol) of 1-SB_9H_9 was quickly added and reduction occurred within 10 s giving a yellow solution. Subsequent treatment of this solution depended upon the nature of the experiment. Concentration of the solution by vacuum evaporation of the solvent afforded an NMR sample.

A separate experiment was conducted in which 10 ml of THF containing 1.1 mmol of sodium naphthalide was added dropwise by an equalized pressure addition funnel to a stirred 10 ml THF solution containing 1.1 mmol of 1-SB_9H_9. The rate of addition was such that each drop of sodium naphthalide solution was completely decolorized before further addition (approximately 10 s between drops). The resulting pale yellow solution was stirred 8 h and concentrated to ca. 2 ml by vacuum evaporation and a NMR sample prepared. The remaining THF was removed by vacuum and the residue Soxhlet extracted 3 h with petroleum ether. Gas chromatography of the extracted material showed it to be about a 2:1 mixture of naphthalene to 1-SB_9H_9.

Complete removal of the solvent from the crude reduced 1-SB_9H_9, washing several times with dry benzene, and Soxhlet extraction of the resulting yellow solid with petroleum ether (bp 30-60 °C) for 6 h under nitrogen yielded only naphthalene in the extract (87% recovery as shown by ^1H NMR, infrared spectroscopy, and gas chromatography). The material not extracted, a highly hygroscopic, bright yellow, crusty salt, V, was dissolved in either dimethyl-d_6 sulfoxide or D_2O in the case of NMR analysis. Starting with 320 mg (2.32 mmol) of 1-SB_9H_9, 430 mg of V was obtained (2.33 mmol assuming V to be $Na_2B_9H_9S$). Experiments such as the hydrolysis described above for IV were conducted in the same manner on V.

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The Electron Spin Resonance of Tetra(*p*-carboxylphenyl)porphinatocobalt(II) in Pyridine at 77 K

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Abstract: Electron spin resonance (ESR) spectra of tetra(*p*-carboxyphenyl)porphinatocobalt(II) (Co(*p*-COOH)TPP) in pyridine showed well-resolved superhyperfine (shf) structure due to two nitrogen nuclei from two solvent molecules coordinated to the fifth and the sixth positions of the square planar complex. From these spectra, complete ESR parameters were determined, and an attempt was made to calculate the relative orbital energies of the d orbitals with assumed values of the Racah, the inverse cube radial, and the spin-orbit coupling parameters.

Assour,[1] in 1965, studied the ESR of cobalt phthalocyanine (CoPc) in several heterocyclic amines at 77 K. Shf splittings were observed and were interpreted as due to two N nuclei. The spectra, however, looked more like those due to the complex being coordinated to only one N. Walker,[2] much later, studied the ESR of tetra(*p*-methoxyphenyl)porphinatocobalt (Co(*p*-OCH_3)TPP) in toluene glass in the presence of various concentrations of amines and showed that both five- and six-coordinated complexes could be formed. They were designated as the 1:1 and 2:1 ad-

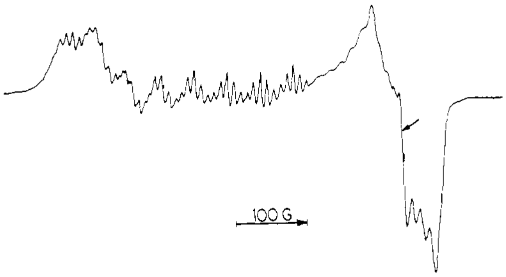

Figure 1. ESR spectrum of tetra(*p*-carboxyphenyl)porphinatocobalt(II) in pyridine in the presence of air.

Table I

	$g_\parallel$	$g_\perp$	$\lvert A_\parallel \rvert$	$\lvert A_\perp \rvert$	$\lvert A_\parallel{}^N \rvert$	$\lvert A_\perp{}^N \rvert$
Co(*p*-OCH$_3$)-TPP (in toluene–pyridine)	2.047	2.216	0.0060	0.0057	—	—
Co(*p*-COOH)-TPP in pyridine	2.054	2.236	0.0053	0.0052	0.0012	0.0010

ducts, respectively. The spectra due to the 1:1 complex bore strong resemblance to those reported by Assour. The 2:1 complexes, on the other hand, had different sets of ESR parameters. The shf structure of the 2:1 complexes was generally not resolved (see Figure 3 of ref 2). Walker[2] also observed that, in the presence of air, a third spectrum appeared which could be interpreted as a six-coordinated complex with one amine and one oxygen molecule.

We wish to report here that, with Co(*p*-COOH)TPP in pyridine, shf structure due to two N could be resolved. The ESR parameters determined from these spectra are similar to those of the 2:1 complexes described by Walker. They can further be used to derive the orbital energy levels from theoretical expressions.

Experimental Section

The synthesis of the free base followed closely that described by Longo et al.[3] From this, the metal complex was prepared by the method of Adler et al.[4] The metal complex was dissolved in pyridine and the concentration was varied until best resolution of the ESR spectra was attained (~0.002 M).

When due care was not taken to exclude air, a spectrum like that shown in Figure 1 was obtained. The eight groups of lines on the low field side are the perpendicular feature of the cobalt hyperfine structure. The 1:2:3:2:1 shf pattern of each group can be interpreted as due to two N from two pyridine molecules. The weak parallel feature of the spectrum could not be seen due to the presence of a strong signal which is characteristic of the oxygen adduct described by Walker. The short arrow in Figure 1 indicates the position of the well-known but little understood "free radical line".

By carefully excluding air, the signal due to the oxygen adduct could be eliminated and a spectrum like that shown in Figure 2 was obtained. Two of the highest field cobalt parallel lines can now be seen with the appropriate shf structure. The single free radical line is again indicated by an arrow in the figure. Aside from this free radical line, the spectrum closely resembles that shown in Figure 3b of ref 2 with the important exception that the N shf structure is well resolved. From this last spectrum all ESR parameters can be determined and are compared with Walker's data for Co(*p*-OCH$_3$)TPP in Table I.

Discussion

Griffith[5] considered three possible cases for the low spin ($S = \frac{1}{2}$) cobalt porphyrins and favored the choice of $^2A_1$ as the ground state with the unpaired electron being in d_{z^2} (a_1 orbital of C_{4v} or D_4). His theoretical expressions do not explicitly take bonding into account but one could consider

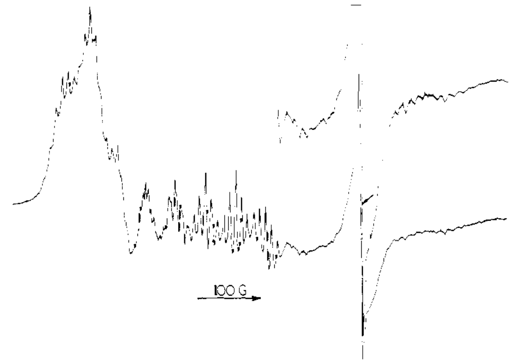

Figure 2. ESR spectrum of tetra(*p*-carboxyphenyl)porphinatocobalt(II) in pyridine in the absence of air.

Table II

	K	$E(b_1) - E(a_1)$, cm^{-1}	$E(b_1) - E(e)$, cm^{-1}	$E(a_1) - E(e)$, cm^{-1}
Calculation I (assuming $A_\parallel > 0$, $A_\perp > 0$):				
Co(*p*-OCH$_3$)TPP	−0.0071	13 500	22 400	8900
Co(*p*-COOH)TPP	−0.0061	14 800	22 400	7600
Calculation II (assuming $A_\parallel > 0$, $A_\perp < 0$):				
Co(*p*-OCH$_3$)TPP	0.0043	15 000	23 900	8900
Co(*p*-COOH)TPP	0.0043	16 000	23 600	7600

the covalency effect as being absorbed in the inverse cube radial parameter P. In our case, since the shf splitting due to N is known, we could, by following a method described by Assour,[1] estimate the square of the bonding coefficient of d_{z^2} in the a_1 MO. This turned out to be 0.99 as compared with 0.97 for CoPc calculated by Assour. We therefore assumed P to be equal to that of the free ion and calculated the isotropic contribution K ($-P\kappa$ in Griffith's expressions) and the relative energy levels of $d_{x^2-y^2}$ (b_1), d_{z^2} (a_1), and d_{xz}, d_{yz} (e) from the three first-order equations for $g_\perp$, $A_\parallel$, and $A_\perp$. The calculations were carried out with assumed values of the Racah electrostatic energy parameters B and C and the spin-orbit coupling parameter ζ. Strictly speaking, Griffith's equations could not be used directly because the mixing coefficients y_i involved energies of states which were not eigenstates of the electrostatic Hamiltonian. We had, in fact, used a modified form of the expressions (see Appendix; eq 2, 3, 4). The results of the calculations with $P = 0.0254$,[6] $B = 1115$, $C = 4366$,[7] and $\zeta = 515$ (cm^{-1})[8] are shown in Table II.

The calculations show that a_1 is above e by about 8000 cm^{-1} as compared with about 2000 cm^{-1} in the case of cobalt porphyrins diluted in free bases.[9] This raising of the energy of a_1 is due to the coordination of solvent molecules to the fifth and the sixth positions of the square planar complex.

To first order, $g_\parallel = 2$ but Griffith[5] also derived a second-order expression for $g_\parallel$, the corresponding modified form being eq 5 of the Appendix. In principle, one could use this equation to calculate the relative orbital energy of d_{xy} (b_2), thus completely establishing the orbital energy scheme. In practice, it turned out that the calculation invariably placed the b_2 orbital too high. This probably was due to the low lying ^4E state (corresponding to Griffith's $E(\psi_2)$) which rendered the treatment by perturbation inappropriate. However, if one assumes a reasonable value of about 25 000 cm^{-1} for $E(b_1) - E(b_2)$ (cf. ref 9 for Cu(*p*-COOH)TPP), one could calculate $g_\parallel$ from the second-order equation and study it in the light of the experimental values. It was found that with both $A_\parallel$ and $A_\perp > 0$ (calculation I) $g_\parallel$ turned out to be >4 while with $A_\parallel > 0$ and $A_\perp < 0$, $g_\parallel$ was approximately 2.1, much larger than the experimental value but nevertheless more reasonable than the other alternative. It is with this conviction that we favor the choice of $A_\parallel > 0$ and $A_\perp < 0$. With this choice, $K = +0.0043$ and, by a method suggested by Symons and Wilkinson,[10] this isotropic contribution corresponds to a 3% admixture of Co 4s orbital.

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Appendix

In the complementary "hole" scheme, the zeroth order Kramer's doublet is:

$$|\psi_0\rangle = \left|\overset{+}{\epsilon}\,\overset{-}{\epsilon}\,\overset{+}{\theta}\right|$$

$$|\psi'_0\rangle = \left|\overset{+}{\epsilon}\,\overset{-}{\epsilon}\,\overset{-}{\theta}\right|$$

The excited states being mixed in through spin-orbit coupling are defined as below:

$$|\psi_1\rangle = \left|\overset{+}{\epsilon}\,\overset{-}{\epsilon}\,\overset{-}{1}\right| \qquad |\psi'_1\rangle = \left|\overset{+}{\epsilon}\,\overset{-}{\epsilon}\,\overset{+}{-1}\right|$$

$$|\psi_2\rangle = \left|\overset{+}{\epsilon}\,\overset{+}{1}\,\overset{+}{\theta}\right| \qquad |\psi'_2\rangle = \left|\overset{-}{-1}\,\overset{-}{\epsilon}\,\overset{-}{\theta}\right|$$

$$|\psi_3\rangle = \left|\overset{+}{\epsilon}\,\overset{-}{\mu}\,\overset{+}{\theta}\right| \qquad |\psi'_3\rangle = \left|\overset{-}{\epsilon}\,\overset{+}{\mu}\,\overset{-}{\theta}\right|$$

$$|\psi_4\rangle = \left|\overset{-}{-1}\,\overset{-}{\epsilon}\,\overset{+}{\theta}\right| \qquad |\psi'_4\rangle = \left|\overset{+}{\epsilon}\,\overset{+}{1}\,\overset{-}{\theta}\right|$$

$$|\psi_5\rangle = \left|\overset{+}{\mu}\,\overset{-}{\epsilon}\,\overset{+}{\theta}\right| \qquad |\psi'_5\rangle = \left|\overset{-}{\mu}\,\overset{+}{\epsilon}\,\overset{-}{\theta}\right|$$

The difficulty in using Griffith's equations lies in the fact that not all the $|\psi_i\rangle$ and $|\psi'_i\rangle$ are eigenstates of the electrostatic Hamiltonian. As a consequence, not all the $E(\psi_i)$'s are well defined, exceptions being $|\psi_1\rangle$, $|\psi'_1\rangle$, $|\psi_2\rangle$, and $|\psi'_2\rangle$. The former two states belong to a ^{2}E and the latter a ^{4}E state. In order to circumvent this difficulty, all single determinantal states from each configuration were first written down and the matrices of the electrostatic Hamiltonian were diagonalized within the configuration (configuration interaction neglected). The results which can also be obtained from Otsuka's work[11] are summarized in Table III.

In this table $V_1 = E(b_1) - E(a_1)$, $V_2 = E(b_1) - E(e)$, $V_3 = E(b_1) - E(b_2)$; B and C are Racah electrostatic energy parameters. The eingenstates are expressed in terms of the single determintal states as follows:

$$|X\rangle = m|x\rangle + n|y\rangle$$

$$|Y\rangle = n|x\rangle - m|y\rangle$$

$$|Z\rangle = \frac{1}{\sqrt{3}}(|a\rangle + |b\rangle + |c\rangle)$$

$$|U\rangle = \frac{1}{\sqrt{6}}(2|d\rangle - |e\rangle - |f\rangle)$$

$$|V\rangle = \frac{1}{\sqrt{2}}(|e\rangle - |f\rangle)$$

$$|W\rangle = \frac{1}{\sqrt{3}}(|d\rangle + |e\rangle + |f\rangle)$$

$$|X\rangle = \frac{1}{\sqrt{6}}(2|a\rangle - |b\rangle - |c\rangle)$$

Table III. The Zeroth Order Energies (and Eigenstates) Relative to the ^{2}A$_1$ Ground State as Zero

Configuration	State	Ligand field energy	Electrostatic energy	Eigenstate designation
$(b_1)^2a_1$	$^2A_1$	0	0	$\lvert\psi_0\rangle$
$(b_1)^2e$	$^2E(1)$	$V_2 - V_1$	$5B$	$\lvert\psi_1\rangle$
	^4E	V_2	$-4(B + C)$	$\lvert\psi_2\rangle$ or $\lvert Z\rangle$
$(b_1)(a_1)(e)$	$^2E(Y)$	V_2	$4B - C - \sqrt{7}B$	$\lvert Y\rangle$
	$^2E(X)$	V_2	$4B - C + \sqrt{7}B$	$\lvert X\rangle$
	$^4A_2$	V_3	$-4(B + C)$	$\lvert W\rangle$
$(b_1)(a_1)(b_2)$	$^2A_2(V)$	V_3	$-C$	$\lvert V\rangle$
	$^2A_2(U)$	V_3	$8B - C$	$\lvert U\rangle$

$$|Y\rangle = \frac{1}{\sqrt{2}}(|b\rangle - |c\rangle)$$

$$m = [27/(56 + 4\sqrt{7})]^{1/2}$$

$$n = [(29 + 4\sqrt{7})/(56 + 4\sqrt{7})]^{1/2}$$

The eigenstates, $|X'\rangle, |Y'\rangle, |Z'\rangle, |U'\rangle, |V'\rangle, |W'\rangle$ which are associated with the Ms = $-\frac{1}{2}$ zeroth order state $|\psi'_0\rangle$ have similar functional dependence on $|a'\rangle$, etc. The single determinantal states $|a\rangle$, etc., are defined as:

$$|a\rangle = \left|\overset{-}{\epsilon}\,\overset{-}{-1}\,\overset{+}{\theta}\right| \qquad |b\rangle = \left|\overset{-}{\epsilon}\,\overset{+}{-1}\,\overset{-}{\theta}\right| \qquad |c\rangle = \left|\overset{+}{\epsilon}\,\overset{-}{-1}\,\overset{-}{\theta}\right|$$

$$|d\rangle = \left|\overset{+}{\epsilon}\,\overset{+}{\mu}\,\overset{-}{\theta}\right| \qquad |e\rangle = \left|\overset{+}{\epsilon}\,\overset{-}{\mu}\,\overset{+}{\theta}\right| \qquad |f\rangle = \left|\overset{-}{\epsilon}\,\overset{+}{\mu}\,\overset{+}{\theta}\right|$$

In terms of the eigenstates, the first-order Kramer's doublet is found to be:

$$|+\rangle = \eta_0|\psi_0\rangle - \frac{\sqrt{6}}{2}\frac{\zeta}{E(^2E(1))}|\psi_1\rangle - \frac{1}{\sqrt{2}}\frac{\zeta}{E(^4E)}|\psi_2\rangle + \frac{m}{\sqrt{3}}\frac{\zeta}{E(^2E(X))}|X\rangle + \frac{n}{\sqrt{3}}\frac{\zeta}{E(^2E(Y))}|Y\rangle + \frac{1}{\sqrt{6}}\frac{\zeta}{E(^4E)}|Z\rangle - \sqrt{\frac{2}{3}}\frac{\zeta}{E(^2A_2(U))}|U\rangle + \frac{2}{\sqrt{3}}\frac{\zeta}{E(^4A_2)}|W\rangle$$

The state $|-)$ has similar functional dependence on the primed states.

In terms of the single determinantal states, the first-order Kramer's doublet becomes:

$$|+\rangle = \eta_0|\psi_0\rangle + \eta_1|\psi_1\rangle + \eta_2|\psi_2\rangle + \eta_3|a\rangle + \eta_4|b\rangle + \eta_5|c\rangle + \eta_6|d\rangle + \eta_7|e\rangle + \eta_8|f\rangle$$

and a similar expression for $|-\rangle$. In these expressions,

$$\eta_0 = \left[1 - \sum_{i=1}^{8}\eta_i^2\right]^{1/2}$$

$$\eta_1 = -\sqrt{\frac{3}{2}}\frac{\zeta}{E(^2E(1))} \qquad \eta_2 = -\frac{1}{\sqrt{2}}\frac{\zeta}{E(^4E)}$$

$$\eta_3 = \frac{\zeta}{3\sqrt{2}}\left\{\frac{1}{E(^4E)} + \frac{2m^2}{E(^2E(X))} + \frac{2n^2}{E(^2E(Y))}\right\}$$

$$\eta_4 = \frac{\zeta}{3\sqrt{2}}\left\{\frac{1}{E(^4E)} - \frac{m^2 - \sqrt{3}mn}{E(^2E(X))} - \frac{n^2 + \sqrt{3}mn}{E(^2E(Y))}\right\}$$

$$\eta_5 = \frac{\zeta}{3\sqrt{2}}\left\{\frac{1}{E(^4E)} - \frac{m^2 + \sqrt{3}mn}{E(^2E(X))} - \frac{n^2 - \sqrt{3}mn}{E(^2E(Y))}\right\}$$

$$\eta_6 = \frac{2\zeta}{3}\left\{\frac{1}{E(^4A_2)} - \frac{1}{E(^2A_2(U))}\right\}$$

$$\eta_7 = \eta_8 = \frac{\zeta}{3}\left\{\frac{2}{E(^4A_2)} - \frac{1}{E(^2A_2(U))}\right\}$$

A somewhat simpler form assumes that the two ^{2}E states from the $(b_1)(a_1)(e)$ configuration have equal energies, i.e.,

${}^2E(X) = {}^2E(Y) = {}^2E(2) = 4B - C$. With this assumption,

$$\eta_4 = \eta_5 = \frac{\zeta}{3\sqrt{2}}\left\{\frac{1}{E({}^4E)} - \frac{1}{E({}^2E(2))}\right\}$$

From the above expressions for the Kramer's doublet, the equations for $g_\parallel$, $g_\perp$, $A_\parallel$, and $A_\perp$, correct to first order, are found to be:

$$g_\parallel = 2 \tag{1}$$

$$g_\perp = 2 - \frac{6\zeta}{E({}^2E(1))} \tag{2}$$

$$A_\parallel = -K + \frac{P}{7}\left\{4 + \frac{6\zeta}{E({}^2E(1))} + 4\zeta\left[\frac{1}{E({}^4E)} - \frac{1}{E({}^2E(2))}\right]\right\} \tag{3}$$

$$A_\perp = -K - \frac{P}{7}\left[2 + \frac{45\zeta}{E({}^2E(1))}\right] \tag{4}$$

where $K = P\kappa$.

The second-order equation for $g_\parallel$ calculated from the formula, $2\langle +|Lz + 2Sz|+\rangle$, turned out to be independent of the energies of ${}^4A_2$ and ${}^2A_2$ although the first-order expression for the Kramer's doublet contains them. Additional second-order contribution to $g_\parallel$ comes from second-order state functions. The complete second-order equation for $g_\parallel$ turns out to be dependent on the energy of ${}^2A_2(V)$. Thus,

$$g_\parallel = 2 - \frac{3\zeta^2}{\{E({}^2E(1))\}^2} + 2\zeta^2\left[\frac{1}{\{E({}^4E)\}^2} - \frac{1}{\{E({}^2E(2))\}^2}\right] + \frac{8\zeta^2}{3E({}^2A_2(V))}\left[\frac{1}{E({}^4E)} - \frac{1}{E({}^2E(2))}\right] \tag{5}$$

The zeroth-order energies in these equations are functions of the Racah parameters, B and C, and the ligand field parameters, V_1, V_2, and V_3. Besides these, K and P, corresponding to the isotropic and the anisotropic nuclear hyperfine interactions, are also unknown. When the covalency effect is not large we may use the free ion values for B, C, P, and ζ, and calculate K, V_1, V_2, and V_3. Although admittedly the orbital energies thus calculated are only approximate, it is nevertheless well known that for porphyrin complexes, where d–d transitions are masked by strong π–π^* transitions, such information could not be obtained through other means, such as optical studies.

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Intramolecular Ligand Exchange in Phosphoranes. A Comparison of Berry Pseudorotation and Turnstile Rotation

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Abstract: Ab initio calculations employing a large basis set have been carried out for a model molecule (PH_5) to investigate the reaction profiles corresponding to the Berry pseudorotation (BPR) and the turnstile rotation (TR), these being the mechanistic possibilities proposed for the intramolecular ligand exchange in phosphoranes. Results suggest that the BPR should be a concerted process involving a very low (1.95 kcal/mol) energy of activation. In contrast, the TR process, which could be the active reaction coordinate for structurally restricted systems, may be better described as a sequential type process with a considerably larger (10.05 kcal/mol) overall activation energy. Examination of the reaction hypersurface in the vicinity of the C_s and C_{4v} points revealed that only the C_{4v} geometry represents a genuine saddle point. This implies that, at least in the case of structurally flexible phosphoranes as modeled by PH_5, the TR should be regarded as a vibrationally excited mode of the BPR.

The exchange of ligands around pentacoordinate phosphorus in phosphoranes of the type PX_5, where X may be aryl or halogen, has been the subject of a wide variety of investigations.[1] Two mechanisms have been proposed to account for the observed exchange: the Berry pseudorotation (BPR)[2] and the turnstile rotation (TR)[3] process as illustrated in Scheme I. Although these mechanistic alternatives involve entirely different molecular motions, it has not been possible hitherto to distinguish between them experimentally.[4] On the other hand, quantum-mechanical calculations, both semiempirical[5] and ab initio,[6] have shown that the energy of activation for the BPR process is considerably lower than that of the TR process and thus should be favored. However, there has been no attempt so far to investigate the reaction profile of these processes in detail[7] in order to obtain information with regards to their synchronous or stepwise nature. Furthermore, no consideration has been given to the interrelationship of the TR and BPR modes, which is of considerable importance regarding the experimental distinguishability of these mechanistic alternatives.