fragment which retains the charge, whereas the C-1 methylene group is eliminated in the neutral. Thus, if the ionic fragment also had the ethene structure,[5] the labeling evidence would indicate that the charge was being retained by one ethene moiety in preference to the other. Such behavior would hold implication as to relative rates of atomic and electronic reorganizations not easily justified on theoretical grounds. The ionic fragment could, however, correspond to $(CH_3CH)^{+\cdot}$, which has been detected in charge exchange experiments[6] and whose heat of formation has been estimated as being 40 kJ mol^{-1} above that of $(CH_2{=}CH_2)^{+\cdot}$.[7] The results now point directly to a mechanism[8] (eq 1). The charge retention is explained if the activation energy for formation of $(CH_3CH)^{+\cdot}$ and $CH_2{=}CH_2$ is significantly lower than that for formation of CH_3CH and $(CH_2{=}CH_2)^{+\cdot}$. This is true as long as the processes do not have large reverse activation energies, since their heats of reaction are 280 and 580 kJ mol^{-1}, respectively.[9] The second step of the process 1 is supported by FIK measurements on methylcyclopropane.[2k] These show a rapid loss of ethene whose rate steadily increases on moving to shorter times (from ns to 20 ps), i.e., no inflection in the rate/time curve. This behavior is consistent with loss of ethene from the methylcyclopropane radical cation without rearrangement or prior isomerization.

The process depicted in eq 1 provides a link between the branched and straight-chain acyclic $(C_4H_8)^{+\cdot}$ species.[10] Radiolysis experiments have shown that methylcyclopropane ions isomerize to but-2-ene ions and to a lesser extent to 2-methylpropene ions.[2c,f] Similarly FIK measurements suggest that methylcyclopropane and but-2-ene ions isomerize to a common structure or mixture of structures prior to decomposition in 40 ps.[2k] Indeed the conversion of the methylcyclopropane to the but-2-ene ion could be achieved by a process exactly analogous to the first step of the process depicted in eq 1 (i.e., 1,2-hydrogen shift and the swiveling of a C-C bond). Thus, given the conversion of the 2-methylpropene ion to the methylcyclopropane ion as in eq 1, a further similar step can convert the methylcyclopropane to the but-2-ene ion and the link is forged between the linear and branched $(C_4H_8)^{+\cdot}$ isomers.

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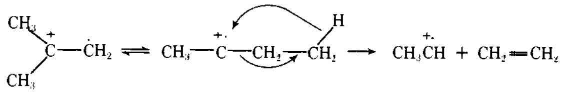

$$(CH_3)_2\overset{+}{C}{-}\dot{C}H_2 \rightleftharpoons CH_3{-}\overset{+\cdot}{C}{-}CH_2{-}CH_2{-}H \longrightarrow CH_3\overset{+\cdot}{C}H + CH_2{=}CH_2$$

(9) The heats of formation used in calculating these heats of reactions are 870 kJ mol^{-1} for $((CH_3)_2C{=}CH_2)^{+\cdot}$ (F. P. Lossing, *Can. J. Chem.*, **50**, 3973 (1972)), 52 kJ mol^{-1} for $CH_2{=}CH_2$, 1100 kJ mol^{-1} for $(CH_3CH)^{+\cdot}$ (ref 6 and 7), 390 kJ mol^{-1} for $CH_3\ddot{C}H$ (J. A. Altmann et al. in ref 4), and 1060 kJ mol^{-1} for $(CH_2{=}CH_2)^{+\cdot}$.

(10) The transition state bears analogy to the well-documented protonated cyclopropane $(C_3H_7)^+$ system. Molecular orbital calculation (P. C. Hariharan, L. Radom, J. A. Pople, and P. v. R. Schleyer, *J. Am. Chem. Soc.*, **96**, 599 (1974)) indicates that the edge protonated cyclopropane ion has an energy 25 kJ mol^{-1} above that of the corner-protonated and 21 kJ mol^{-1} above that of the 1-propyl. Gas-phase experiments suggest that protonated cyclopropane is a stable species with a heat of formation 29–38 kJ mol^{-1} above that of the 2-propyl ion (D. J. McAdoo, F. W. McLafferty, and P. F. Bente, *ibid.*, **94**, 2027 (1972); S.-L. Chong and J. L. Franklin, *ibid.*, **94**, 6347 (1972)). The mechanism to explain hydrogen and carbon scrambling in superacid solution involves edge-protonated cyclopropane ions as transition states between corner-protonated species (M. Saunders, P. Vogel, G. L. Hagan, and J. Rosenfeld, *Acc. Chem. Res.*, **6**, 53 (1973)). See also P. P. Dymerski, R. M. Prinstein, P. F. Bente III, and F. W. McLafferty, *J. Am. Chem. Soc.*, **98**, 6834 (1976).

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Direct Raman Evidence for Resonance Interactions between the Porphyrin Ring System and Ring-Conjugated Substituents in Porphyrins, Porphyrin Dications, and Metalloporphyrins

Sir:

Many porphyrins and metalloporphyrins contain unsaturated substituents which appear from structural formulae to be conjugated with the porphyrin ring system—(1) vinyl and/or acyl groups bound to pyrrole carbons (β substituents) in biological porphyrins and (2) phenyl and other aryl groups bound to bridging methine carbons (meso substituents) in synthetic tetraarylporphines—but the extent and significance of π delocalization linking the porphyrin ring system with unsaturated β and meso substituents is not at all obvious. The pyrrole β-carbon-β-carbon bonds in porphyrins are significantly shorter than other more clearly benzenoid carbon-carbon bonds.[1,2] Although a simple averaging of canonical forms of porphyrin dianions or metalloporphyrins indicates a β-β bond order of 1.75, which can account for the relatively short β-β bonds without ruling out involvement of the β carbons in the delocalized porphyrin π system, the apparent isolated double-bond character[2] of the β-β bond raises doubts about π delocalization that links the porphyrin ring system with unsaturated β substituents. Molecular orbital calculations describing the π systems of porphyrins and metalloporphyrins have been based upon the assumption that the β-β bonds are isolated double bonds; calculations have focussed on the inner 16 atom, 18-π-electron ring that excludes the β carbons.[3] The lack of coplanarity between the porphyrin ring system and *meso*-aryl groups raises doubts about π delocalization that links the porphyrin ring system with *meso*-aryl substituents. Dihedral angles between the porphyrin ring system ,average plane and *meso*-aryl substituent planes range from ~20° for porphyrin dications through ~60° for neutral, metal-free

Table I. Halogen-Sensitive Infrared and Resonance Raman Bands (cm^{-1}) in Spectra of Tetra(halophenyl)porphine and Related Compounds[a]

	o-Cl	*p*-Cl[b]	*p*-Br[b]	*p*-I
Substituted benzene[c]		1085 (IR)	1070 (IR)	1060 (IR)
		1083 (R)	1071 (R)	1060 (R)
Substituted toluene	1054 (IR)[d,e]	1092,[d] 1090[e] (IR)	1069,[d] 1071[e] (IR)	1061 (IR)[d]
TXPP solid	1058 (IR)	1092 (IR)	1071 (IR)	1058 (IR)
		nd (RR)	nd (RR)	1061 sh (RR)[f]
TXPP dication·$2CF_3COO^-$ solid[g]		1096 (IR)	1072 (IR)	1060 (IR)
		1094 sh (RR)	nd (RR)	1060 (RR)
TXPP dication·$2CF_3COO^-$ in $CHCl_3$ solution	nd (RR)	1096 (RR)	1076 (RR)	1061 (RR)
Cu(II) TXPP solid		1091 (IR)	1072 (IR)	1060 (IR)
		1090 sh (RR)	nd (RR)	1061 sh (RR)[h]

[a] Abbreviations used: IR, infrared; R, Raman; RR, resonance Raman; TXPP, tetra(halophenyl)porphine; nd, not detected; sh, shoulder. [b] Chlorin-free porphyrins. [c] Reference 19a. [d] Reference 19c. [e] Reference 19d. [f] C analysis was low (calcd 47.3%, found 46.1%). [g] C, H analyses were low and F analysis (on TPP dication) was high, consistent with contaminating CF_3COOH but not contaminating neutral porphyrin. [h] C analysis was high (calcd 44.8%, found 46.6%), but optical spectra showed no evidence of contaminating metal-free porphyrin.

porphyrins to ~80° for metalloporphyrins.[2] Resonance energy calculations for tetraphenylporphin have been based upon the assumption that the *meso*-phenyl groups are independent of the π system of the porphyrin ring.[4]

Despite theoretical doubts about π delocalization linking the porphyrin ring system with unsaturated substituents, there is indirect experimental evidence for such delocalization. π delocalization involving β-acyl groups has been used to rationalize an infrared probe of the state of iron in iron porphyrins.[5] β-Acetyl groups in a crystalline nickel(II) porphyrin are coplanar with the porphyrin ring system.[6] Linear free-energy correlations are consistent with π delocalization linking the porphyrin ring system to *meso*-phenyl groups,[7] although an alternative interpretation has been offered[8] for some of the correlations. There is direct magnetic resonance evidence for the linking of *meso*-phenyl groups to the delocalized porphyrin ring systems of copper and iron porphyrins.[9] There is need for further direct and unambiguous evidence that bears on the extent of π delocalization in porphyrin compounds.

We here present the results of resonance Raman studies which directly demonstrate π delocalization linking β-acyl groups with the porphyrin ring system and which directly and independently confirm the previous evidence that *meso*-phenyl groups are linked to the porphyrin ring system through π delocalization. Our results challenge assumptions involved in molecular orbital and resonance energy calculations on porphyrins and underscore the potential usefulness of vibrational spectroscopic probes in characterizing porphyrins, metalloporphyrins, and heme proteins.

Resonance Raman spectroscopy of porphyrins and their derivatives can offer direct qualitative evidence for significant π delocalization involving ostensibly conjugated substituents because resonance enhancement of Raman scattering occurs only when the excited vibrations involve atoms which are part of the delocalized chromophore.[10] Previous resonance Raman studies involving protoporphyrin derivatives could not unambiguously demonstrate whether the β-vinyl groups were part of the delocalized π system because of difficulties in assigning the C=C stretching frequency associated with the vinyl group.[11] Previous resonance Raman studies involving tetraphenylporphine derivatives[12] have not dealt with the question of whether excitation of phenyl group vibrations occured during resonance Raman experiments.

Resonance Raman spectra were obtained by irradiation of spinning porphyrin samples with the 457.9-nm line of an Ar^+ laser. The wavelength of irradiation corresponded to a region of intense Soret band absorption (in tetraarylporphine dications) or to the region of near minimal but nonzero absorbance on the long wavelength side of the Soret band (in other species). The following were evidence that the Raman spectra obtained were resonance enhanced: (1) the relatively low porphyrin concentrations necessary (~10^{-3} M in solution and ~10^{-6} mol in the solid), (2) the absence of C-H stretching bands and nonconjugated ester carbonyl stretching bands which are Raman active.

Resonance Raman spectra of porphyrin dications have not been reported previously. Solutions of dications of tetraarylporphines and octaethylporphine, formed by addition of excess trifluoroacetic acid to porphyrin solutions in chloroform or other halocarbon solvents, exhibited resonance Raman spectra which were almost free of fluorescence effects. Solutions of dications of deuteroporphyrin dimethyl ester and 2,4-diacetyldeuteroporphyrin dimethyl ester did not yield satisfactory spectra under the same conditions.

Porphyrins and metalloporphyrins were prepared by standard methods.[13] Tetra(*p*-iodophenyl)porphine was subjected to additional chromatography. Octaethylporphine was purchased from Strem Chemicals, Danvers, Mass. Chlorin-free tetraarylporphines were prepared by quinone oxidation of contaminating chlorins.[14] Evaporation of solvent from trifluoroacetic acid solutions of porphyrins produced solid porphyrin dication salts. All compounds, except those specifically labeled in Table I, exhibited satisfactory C, H analyses.

Delocalization Involving β Substituents. Neutral, metal-free 2,4-diacetyldeuteroporphyrin dimethyl ester in the solid in KBr exhibited a resonance Raman acetyl carbonyl stretching band at ~1660 cm^{-1}. Solid μ-oxo-bis[porphinato]iron(III) and bis[pyridinoporphinato]iron(II) derivatives of the same porphyrin exhibited resonance Raman acetyl carbonyl stretching bands at 1654 and 1644 cm^{-1}, respectively. The acetyl carbonyl stretching frequencies correspond well to the reported values obtained from infrared data on chloroform solutions.[5] These results indicate significant π delocalization linking β-acetyl substituents with the porphyrin ring system. Resonance Raman spectra of chlorophyll b,[15] which also contains β-acyl groups, indicate that π delocalization involving β-acyl groups also occurs in chlorin ring systems. Our results suggest that β-vinyl groups in the hemes of heme proteins also are linked through π delocalization to porphyrin ring systems, with possibly significant consequences[16] for heme-protein interactions, since β-vinyl groups appear to interact with aromatic amino acid side chains in myoglobin.[17] Our results indicate that treatment of porphyrins as single ring π systems is an oversimplification.

Delocalization Involving Meso Substituents. Bands which are associated with carbon-halogen stretching vibrations were detected in the resonance Raman spectra of three tetra(*p*-halophenyl)porphines and their derivatives. Comparisons of solution resonance Raman spectra of the trifluoroacetate dications of tetraphenylporphine (TPP), tetra(*p*-fluorophenyl)-

porphine (TpFPP), tetra(*p*-chlorophenyl)porphine (TpClPP), tetra(*p*-bromophenyl)porphine (TpBrPP), and tetra(*p*-iodophenyl)porphine (TpIPP) indicated medium-strength halogen-sensitive bands in the 1050–1100-cm^{-1} region for TpClPP, TpBrPP, and TpIPP. These bands corresponded to relatively strong infrared bands and relatively weak resonance Raman bands or shoulders in spectra of solid porphyrin dications, solid neutral porphyrins, and solid copper(II) porphyrins (Table I). The same bands have been reported previously as halogen-sensitive infrared bands of TpClPP and TpBrPP[18] and are found in the infrared and Raman spectra of all chlorine-, bromine-, and iodine-containing benzenes and asymmetrically para-disubstituted benzenes[19] (see Table I for examples). Most investigators[19a,c-e] assigned these bands to phenyl ring vibration modes which involve significant extents of C–X stretching motion. Reported[18] fluorine-sensitive bands could not be tested for in resonance Raman spectra because of interfering bands common to all of the tetraarylporphines examined, but TpFPP as well as TPP served as control compounds for comparisons with TpClPP, TpBrPP, and TpIPP. (To further test the correlations, we examined the infrared spectrum of solid tetra(*o*-chlorophenyl)porphine (ToClPP) for a halogen-sensitive band predicted from the infrared and Raman spectra[19c,d] of ortho-disubstituted, chlorine-containing benzene derivatives; the predicted band was observed in the infrared spectrum of the neutral porphyrin but not in the resonance Raman spectrum of the dication in solution. Perhaps *o*-chloro steric effects in ToClPP force the porphyrin–phenyl dihedral angles to close to 90°, thus minimizing π delocalization.) The assignment of 1050–1100-cm^{-1} region halogen-sensitive bands to phenyl ring vibrations which have appreciable C–X stretching character has been confirmed for *p*-chlorofluoro-, *p*-bromofluoro-, and *o*-chlorofluorobenzene by normal coordinate analysis; the normal coordinate analysis did not include iodine-containing compounds.[20] Earlier workers[21] had assigned infrared bands in the 490–510-cm^{-1} region to C–Cl stretching vibrations in TpClPP and metallo TpClPP derivatives by analogy to the infrared spectra of aliphatic compounds; bands in this region instead may be associated with vibrations involving significant C–Cl bending character.[20] Lack of consistency in literature assignments[19,20] of vibrational frequencies associated with halogen motion in meta-disubstituted halogen-containing benzenes precluded our use of tetra(*m*-halophenyl)porphines.

The resonance Raman results provide direct evidence for π delocalization linking *meso*-aryl groups to the porphyrin ring system in porphyrin dications, neutral porphyrins, and copper(II) porphyrins. These results are consistent with previous experimental[7,9a] and calculational[22] evidence. Apparently even dihedral angles over 80° do not preclude π delocalization. Magnetic resonance studies on iron(III) porphyrins[9b] and linear free-energy correlations for nickel(II), vanadyl(IV), and cobalt(II) porphyrins[23] suggest that other metalloporphyrins will exhibit resonance Raman bands associated with *meso*-phenyl substituents. Our results indicate that neither bonding nor resonance energy calculations should ignore π delocalization involving phenyl substituents in tetraarylporphines.

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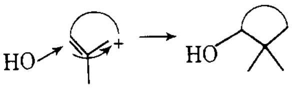
Seven-Membered Rings via Silyl Enol Ether Participation in the Olefin Cyclization. Anti-Markownikoff Cyclization in Biomimetic Terpene Synthesis

Sir:

In light of the crucial role of anti-Markownikoff cyclization in terpene biosynthesis (eq 1), of which enzymic formations of karahanaenone,[1] humulene,[2] and lanosterol (C ring)[3] are the most notable examples, it is surprising that there seems to be no appropriate chemical precedent for such processes. We have been intrigued for some time in the possibility of terminating cationic cyclization via nucleophilic participation of silyl enol ether which, if successful, would result in the formation of several cyclic terpenes otherwise directly unattainable.[4] The present communication describes the initial results which show the feasibility and some limitations of this methodology.



(1)

Since neryl acetate has been shown to undergo facile organoaluminum-promoted cyclization to give a good yield of limonene,[5] we selected to examine the cyclization of the acetate **1** using several different organoaluminum reagents. In that event, it was not clear a priori, whether there would be a preference for formation of a seven- or five-membered ring via the primary or tertiary cation, respectively.