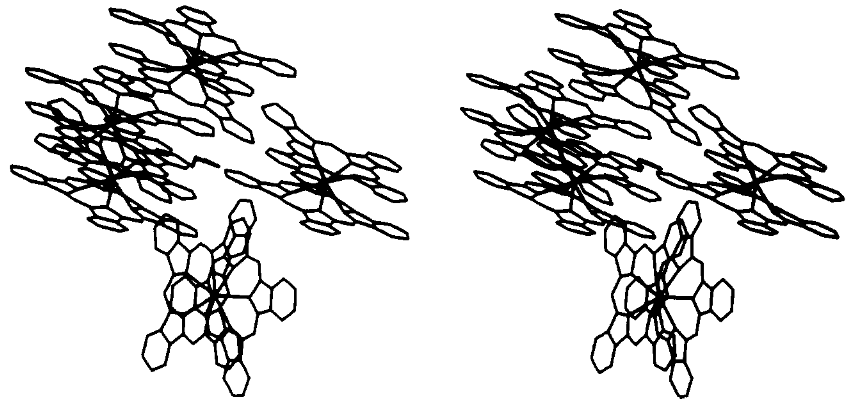

Figure 3. Stereoscopic view of molecular packing cell of the structure.

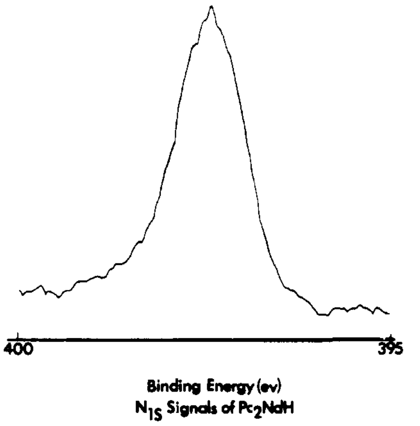

Figure 4. An N 1s X-ray photoelectron spectrum of bis(phthalocyaninato)neodymium(III).

However, the molecules are packed in a three-dimensional "herringbone" pattern (Figure 3) with the molecule of solvation, dichloromethane, on the pseudomirror plane and between the benzimidazole rings of translationally related molecules; it is these rings which show the greatest distortion from symmetry.

One may therefore conclude that the hydrogen occurs at this locus of asymmetry. In order to verify the location of the acidic hydrogen in the complex, we also obtained an N 1s X-ray photoelectron spectrum (Figure 4).[6] The spectrum shows a sharp, single peak (at 398.8 eV with the width of 1.1 eV) in analogy with the spectra of usual types of metallophthalocyanines.[7] The data imply that eight central nitrogen atoms are chemically equivalent to each other, and thereby the acidic hydrogen does not bind strongly to any of the nitrogen atoms in the complex, as opposed to the structure proposed by Nicholson and Galiaridi (Figure 1), though a possibility of a weak interaction between the hydrogen atom and the nitrogen atom(s) cannot be excluded. Recently, Moskalev et al. proposed a double-sandwich model of the neodymium(III) complex, $PcNd^{(III)}Pc(\mu\text{-}H)_2PcNd^{(III)}Pc$, to explain electrochromism.[8] In their model, the acidic hydrogen has a weak intermolecular hydrogen bond, consistent with the result of the N 1s spectrum. Although the position of the acidic hydrogen of the complex could not be detected distinctly in this study, it is elucidated that the two phthalocyanine ring systems form the sandwich-type compound with the neodymium atom in the center and are oriented in the staggered configuration. We are studying electrochromism of bis(phthalocyaninato)neodymium(III) in further detail by using ESR and cyclic voltametry, and the results will be described in a forthcoming paper.

Acknowledgments. We are grateful for support of this work by the Office of Naval Research (Grant 3210) and the Robert A. Welch Foundation (Grants A328, A420, and A614).

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Importance of Solvation on the Gas-Phase Proton-Transfer Reaction between Cyclopentadienyl Anion and Alcohols

Sir:

The reactions of gas-phase ion-neutral clusters, $(IN)^{\pm}$, are of considerable interest since they may bridge the chemistry of these ions in gas- and condensed-phase processes. Most research in this area has involved studies of the association and clustering equilibria (eq (1-3)).[1] Recent reports by several investigators have demonstrated the mediating effect of solvent molecules on the intrinsic properties of gas-phase anions in proton-transfer equilibria[2] and nucleophilic reactivity.[3] We wish to report a "contrathermodynamic" protonation reaction which occurs at a moderate rate because of the role of the "solvent molecule" on the thermochemistry of the overall reaction. This result is directly related to the origin of different acidity scales for proton donors in solution (e.g., in H_2O) and in the gas phase.[4]

$$I^{\pm} + N \rightleftarrows (IN)^{\pm} \tag{1}$$

$$(IN_x)^{\pm} + N \rightleftarrows (IN_{x+1})^{\pm} \tag{2}$$

$$(IN_x)^{\pm} + M \rightleftarrows (IN_{x-1}M)^{\pm} + N \tag{3}$$

Cyclopentadienyl anion, $c\text{-}C_5H_5^-$, was prepared in our flowing afterglow apparatus ($\bar{v} = 80$ m s^{-1}, $P = 0.5$ torr) from the reaction of CH_3O^- with $c\text{-}C_5H_6$ ($\Delta H^\circ_{acid} = 356.1 \pm 2$ kcal mol^{-1})[4] (see eq 4 and 5). Various alcohols were then added downstream of

$$CH_3ONO + e^- \rightarrow CH_3O^- + NO \tag{4}$$

$$CH_3O^- + c\text{-}C_5H_6 \rightarrow CH_3OH + c\text{-}C_5H_5^- \tag{5}$$

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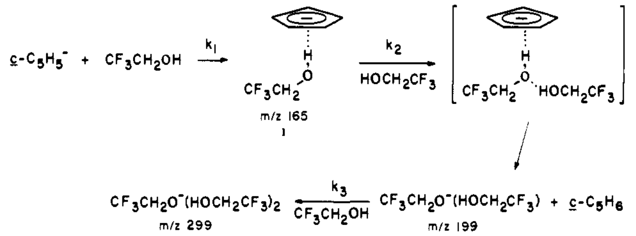
Table I. Summary of Rate Constants and Thermochemical Data for the Reactions of c-$C_5H_5^-$ with Alcohols

alcohol	k_{obsd},[a] cm^3 $molecule^{-1}$ s^{-1}	ΔH°_{acid}, kcal mol^{-1}	ΔH_{rxn} eq 7 for ROH, kcal mol^{-1}
$(CF_3)_2CHOH$	$(1.2 \pm 0.1) \times 10^{-9}$	<351	$\leqslant -5$
CF_3CH_2OH	$(2.7 \pm 0.2) \times 10^{-10}$ [b]	364.4 ± 2	8.3 ± 3
$(CH_3)_3COH$	$(1.5 \pm 0.1) \times 10^{-12}$	373.3 ± 2	17.2 ± 3
C_2H_5OH	$(4.9 \pm 0.2) \times 10^{-12}$	376.1 ± 2	19.8 ± 3
CH_3OH	$(5.9 \pm 0.2) \times 10^{-13}$ [c]	379.2 ± 2	23.1 ± 3

[a] Rate constants are for the decay of c-$C_5H_5^-$ and are estimated to be accurate to ±30%. Errors are standard deviations from multiple determinations. In all reactions, 10^{13} molecules cm^{-3} of Xe was added to the flow just downstream of the electron gun to ensure $He^*(2^3S)$ destruction before the flow reaches the port for ROH addition. [b] This rate constant was found to be independent of P_{He} from 0.5 to 1.1 torr. [c] Measured at $\bar{v} = 52$ m s^{-1}, $P_{He} =$ 0.76 torr.

Scheme I



the ion preparation–thermalization region and the anion products were monitored with a quadrupole mass spectrometer. As expected, the protonation of c-$C_5H_5^-$ by $(CF_3)_2CHOH$ occurred rapidly (see Table I and eq 6) and yielded $(CF_3)_2CHO^-$ (*m/z* 167)

$$\text{c-}C_5H_5^- + (CF_3)_2CHOH \rightarrow \text{c-}C_5H_6 + (CF_3)_2CHO^- \quad (6)$$

$$\Delta H_{rxn} = \delta(\Delta H^\circ_{acids}) < -5 \text{ kcal mol}^{-1}$$

which subsequently attacked a molecule of alcohol to yield the cluster $(CF_3)_2CHO^-(HOCH(CF_3)_2)$ (*m/z* 335).

A somewhat slower reaction was observed between c-$C_5H_5^-$ and CF_3CH_2OH with formation of three product cluster ions, *c*-$C_5H_5^-(HOCH_2CF_3)$ (*m/z* 165), $CF_3CH_2O^-(HOCH_2CF_3)$ (*m/z* 199), and $CF_3CH_2O^-(HOCH_2CF_3)_2$ (*m/z* 299). The rate constant for decay of c-$C_5H_5^-$ and the relative concentrations of ions *m/z* 165 and 199 are independent of P_{He} (0.5–1.1 torr) and flow velocity (80 or 50 m s^{-1}). Initially, it appeared that protonation of c-$C_5H_5^-$ by CF_3CH_2OH had occurred even though the reaction (eq 7) is endoergic. However, we were unable to detect $CF_3CH_2O^-$

$$c\text{-}C_5H_5^- + CF_3CH_2OH \rightarrow c\text{-}C_5H_6 + CF_3CH_2O^- \quad (7)$$

$$\Delta H_{rxn} = \delta(\Delta H^\circ_{acids}) = +8 \pm 3 \text{ kcal mol}^{-1}$$

(*m/z* 99) when CF_3CH_2OH was added, although this alkoxide was readily observed along with its clusters from the CF_3CH_2OH protonation of cyclopentadienylidene anion radical, c-$C_5H_4^{-}$.[5] That reaction 7 *was not occurring* was established by the observation of sequential production of the three cluster ions (Figure 1) while the decay of the signal for c-$C_5H_5^-$ showed pseudo-first-order behavior.[6]

The mechanism for the CF_3CH_2OH–c-$C_5H_5^-$ system (Scheme I) involves initial clustering of c-$C_5H_5^-$ by CF_3CH_2OH to yield **1**, which is considered to be a π-anion hydrogen-bonded complex. Cluster **1** then reacts with another CF_3CH_2OH molecule to yield the homoconjugate alkoxide–alcohol cluster and c-C_5H_6. Further clustering of *m/z* 199 takes place, producing *m/z* 299. It is of special interest that the anion transferred from **1** is that derived from N of $(IN)^-$, not I^-. This anion-switching mechanism accounts for the absence of the unsolvated anion $CF_3CH_2O^-$ (*m/z* 99) in this reaction. Computer fitting of the maxima for ions *m/z* 165 and 199 from Figure 1 yields the rate constants for the three consecutive pseudo-first-order steps of this mechanism,[6] $k_1 = k_3 = {}^1/_2k_2$, where $k_1 = k_{obsd}$, the decay constant for c-$C_5H_5^-$. From the thermochemical cycle (eq 8), the binding energy of cluster

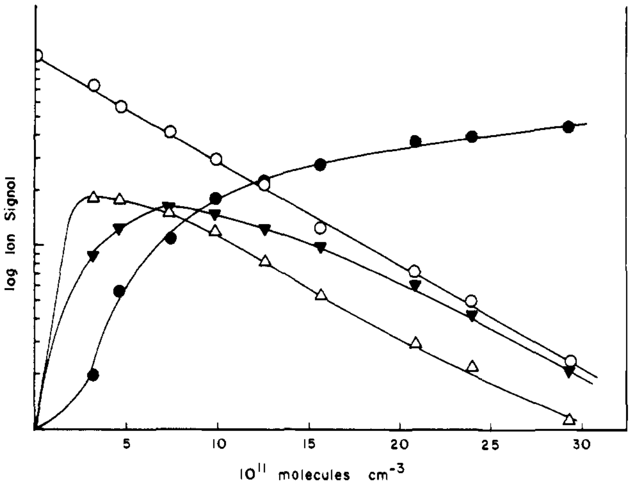


Figure 1. Semilog plot of the decay of c-$C_5H_5^-$ (○) and formation of products (*m/z* 165, △; *m/z* 199, ▲; *m/z* 299, ●) for the reaction of c-$C_5H_5^-$ + CF_3CH_2OH as a function of added alcohol. Ion signals are in arbitrary units.

$$\begin{tikzcd}
\text{c-}C_5H_5^- + ROH \arrow[r] \arrow[d, "a"'] & \text{c-}C_5H_6 + RO^- \\
\text{c-}C_5H_5^-(HOR) \arrow[r, "HOR", "b"'] & \text{c-}C_5H_6 + RO^-(HOR) \arrow[u, "c"', "-HOR"]
\end{tikzcd} \quad (8)$$

1

$$R = CF_3CH_2$$

$CF_3CH_2O^-(HOCH_2CF_3)$ (step b) must be greater than the binding energy of c-$C_5H_5^-(HOCH_2CF_3)$ (step a) by ≥8 ± 3 kcal mol^{-1}.

The c-$C_5H_5^-$ anion also formed 1:1 clusters with $(CH_3)_3COH$, C_2H_5OH, and CH_3OH. However, the anion-switching reactions of these clusters with a second alcohol molecule were not observed and, assuming no third body effects, $k_2 \leq 10^{-13}$ cm^3 $molecule^{-1}$ s^{-1} for these three systems. The endoergicities of the direct proton transfers between c-$C_5H_5^-$ and these alcohols vary from 17 ± 3 to 23 ± 3 kcal mol^{-1}. Apparently, the binding energies of these homoconjugate clusters ($RO^-(HOR)$) are not sufficient to overcome the endoergicity of the proton transfer process. The observed rate constants (Table I) for cluster formation between c-$C_5H_5^-$ and CF_3CH_2OH, C_2H_5OH, and CH_3OH correlate linearly with ΔH°_{acid} of the alcohols.[4] Based on this relationship, the rate constant for c-$C_5H_5^-$ + $(CH_3)_3COH$ is too low, by a factor of 3, probably due to a steric effect to cluster formation with this bulky alcohol. This supports the view that the c-$C_5H_5^-(HOR)$ clusters involve hydrogen bonding between the π-electron cloud of the anion and the alcohol. Observation of **1** and other c-$C_5H_5^-(HOR)$ clusters substantiates recent suggestions that related clusters are intermediates in gas-phase proton transfers[7] to and H-D exchanges[8] with delocalized anions.

The gas-phase results and proposed mechanism for protonation of c-$C_5H_5^-$ by CF_3CH_2OH closely mimic this reaction in solution. This is most evident in the proposed structure of the collision complex of **1** and CF_3CH_2OH (Scheme I). In solution, the proton donor would be the solvate $CF_3CH_2OH(HOCH_2CF_3)_x$ and the

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homoconjugate product would be $CF_3CH_2O^-(HOCH_2CF_3)_x$, both of which are structurally analogous to the species of the ion-cluster steps described here.

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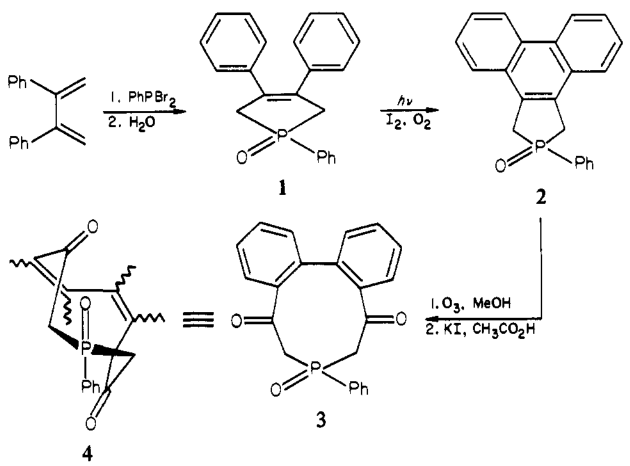
Synthesis of a Dibenzophosphonin

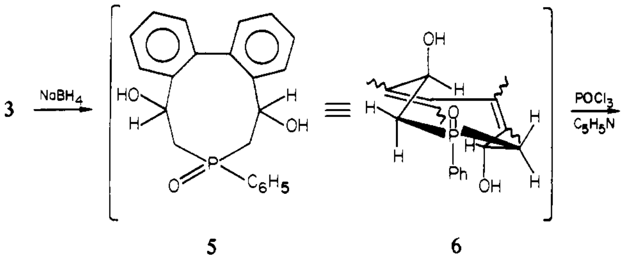
Sir:

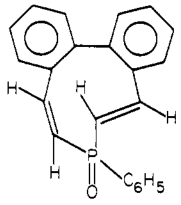
Heterocyclic systems containing ten π electrons (heteronins) are of great theoretical interest and present a formidable synthetic challenge.[1] Of the heteronin systems prepared to date, only the nitrogen[2,3] and oxygen[4,5] compounds have been obtained in monocyclic form, while thionin is known only through annelated derivatives.[6,7] Examples of the phosphonin system have been produced in the form of tetrabenzo derivatives[8] and as the 1,6,9-triphenyl 2,3,4,5-tetracarboxylate,[9] but the heavily substituted nature of these compounds[10] vitiates their usefulness for further study as ten-π-electron systems. Of great need in the study of heteronins, therefore, is a synthetic method suitable for preparing phosphorus representatives which, in view of the results of numerous studies concerning delocalization phenomena in the π-excessive phosphole series,[11] certainly have the potential to exhibit similar effects. We now report the first stepwise synthesis of the phosphonin system, in the form of a dibenzo derivative. The nine-membered-ring intermediates in our synthesis will also be seen to be of interest from a conformational standpoint.

Our synthesis is based upon our previously reported method[12] for the construction of large-ring phosphorus compounds, the ring-opening ozonolysis of a phospholene oxide bearing a cycloalkano ring fused at the double bond. In the present case, the double bond is that at the 9,10 position of phenanthrene, as in **2**. This new system was prepared by photocyclization[13] of 1,3,4-triphenyl-3-phospholene oxide (**1**)[14] by irradiation through a quartz insert with a Hanovia 450-W, high-pressure mercury lamp for 5 h in benzene (56%, mp 197–198 °C).[15] Ozonolysis of **2** in methanol at −40 °C, followed by reductive workup with potassium iodide and acetic acid, afforded the diketone **3** (58%, mp 173.5–174.5 °C; δ ^{31}P +25.9 ($CDCl_3$)). In contrast to the monocyclic parent of the diketophosphonane system whose ^{13}C NMR spectrum indicates a rapid ring inversion at room temperature,[12] compound **3** was found by ^{13}C NMR to exist in an asymmetric conformation that is stable at room temperature, as revealed by the presence of two sets of signals for the carbonyl (δ 194.7 (3.9 Hz) and 194.6 (0 Hz) in $CDCl_3$) and methylene (δ 47.8 (53.7 Hz) and 46.9 (57.6 Hz)) carbons. The asymmetry arises from the chiral phosphorus atom and the inability of the puckered ring with anti carbonyls to undergo ring inversion. This process, which would interchange the carbonyls (and the methylenes also) and thereby cause their equivalence, can only take place over a very high energy barrier, due to the skeletal constraints imposed on the ring by the sites of unsaturation. A likely conformation for the diketone is shown as **4**.



Reduction of **3** with $NaBH_4$ in boiling ethanol gave the diol **5**·C_2H_5OH, mp 262–263 °C, as a single isomer (one ^{31}P NMR signal, +29.9 in Me_2SO). The most likely conformation seems to be **6**, which would result from attack at similar faces of the anti carbonyls of **3**. Dehydration with $POCl_3$ in pyridine at 100 °C for 1 h gave the first phosphonin oxide (**7**, 58%) as a semihydrate, mp 166–167 °C, which is assigned the cis and trans structure from the ^{1}H NMR spectral data (Table I). Thus, there are two different upfield signals for the protons α to P. Each signal is split by the β protons (intermingled with the aromatic protons) but with coupling constants that are drastically different (4 and 14 Hz). The former is in the range for cis protons,[16] the latter for trans. The trans geometry in a nine-membered ring has been encountered for other heteronins[6,17] as well as in 1,2:7,8-dibenzocyclononatetraene.[18] It is notable that attempts to prepare the 1,2:3,4-dibenzocyclononatetraene[19] by dehydration of the diol





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