1,4,7-Triazacycl[3.3.3]azine: Basicity, Photoelectron Spectrum, Photophysical Properties

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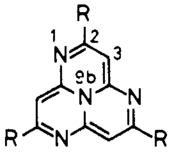
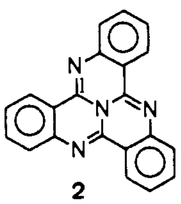
Abstract: 1,4,7-Triazacycl[3.3.3]azine (**1**, R = H) and its 2,5,8-trimethyl derivative **1** (R = Me) are formed in two steps, the condensation of ammonia with acrolein (R = H) or crotonaldehyde (R = Me) and dehydrogenation of the product on Pd/C catalyst. The symmetrical (C_{3h}), purple-colored heterocycles **1** have been characterized by spectroscopic methods (^{1}H and ^{13}C NMR, ESR of the radical anions, PES, and UV/vis absorption and emission). Parent **1** (R = H) is moderately soluble and stable in all solvents from hexane to water, and the three peripheral N atoms are sequentially protonated in increasingly acidic solutions (pK_a = 3.46, −2.2, −7.2). A pronounced blue shift of the first absorption band is observed with increasing solvent polarity, with increasing protonation, upon methyl substitution (**1**, R = H → R = Me), and even upon fusion with three benzo groups (**1** → tricycloquinazoline (**2**)). Compounds **1** give rise to a weak blue fluorescence emission from the second $\pi\pi^*$ excited singlet state S_2, $\phi_f = (5 \pm 1) \times 10^{-4}$ (R = H), $\phi_f \simeq 1 \times 10^{-4}$ (R = Me), as well as a very weak red fluorescence from S_1. The energy gap between the lowest $\pi\pi^*$ excited singlet and triplet states, S_1 and T_1, is very small ($\Delta E < 10$ kJ/mol) and the lifetime of T_1 is unusually short ($^3\tau < 1$ μs). A simple MO model describing the π-electronic structure of cycl[3.3.3]azines serves well to rationalize the physical and chemical properties of the triaza derivatives **1**.

There has been a considerable surge of interest in the synthesis, reactivity, electronic structure (spectroscopy), and biological activity of cycl[3.3.3]azine[1] derivatives (review articles,[2] recent key references[3-10]). Remarkably, the highly symmetrical (C_{3h}) 1,4,7-triazacycl[3.3.3]azine **1**[1] has been largely neglected. This is all the more surprising, since a facile, two-step synthesis of the 2,5,8-trimethyl derivative **1** (R = Me) was reported as early as 1946 in the thesis of Mrazek.[11] Furthermore, the same compound, formed by the same procedure, as well as several derivatives including parent **1** (R = H) were claimed as an invention in a 1963 patent by Van Winkle.[12] However, these compounds were poorly characterized. E.g., the only physical data given for **1** (R = H) are a melting point of "about 95 °C"[12] (this work: 219-220 °C) and an "approximate composition of $C_9H_8N_4$"[13] (actually:



1 (R=H,Me)



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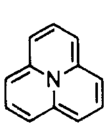

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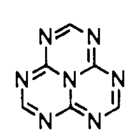

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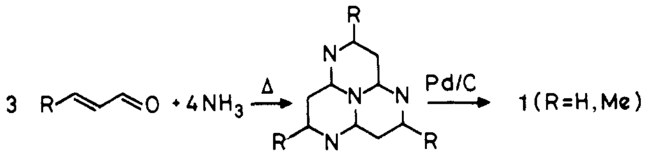
These rudimentary observations[11-13] have hardly received further attention[14] or mention[15] and have not found their way into any of the reviews of cyclazine chemistry.[2] In contrast, the carcinogenic tribenzo derivative of **1**, "tricycloquinazoline" (**2**), has been studied extensively.[16,17] Some time ago we have established that the simple two-step procedure (Scheme I) first described by Mrazek[11] and apparently rediscovered independently by Van Winkle[12,13] indeed yields the cyclazines *1* (R = H, Me) in fair (40%, R = Me) and poor (4%, R = H) yield, respectively.[18] This work has triggered a thorough investigation on the chemical reactivity of **1** (R = Me).[10] We now report a study of these remarkably stable heterocycles focusing on spectroscopic and photophysical properties and on the protonation equilibria of **1** (R = H) in aqueous sulfuric acid. The comparison of **1** with parent cycl[3.3.3]azine (**3**)[3,4,19,20] and the recently synthesized

Scheme I



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‡ University of California at San Diego.

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hexaaza derivative tri-*s*-triazine (**4**)[5–7] provides a revealing exercise in simple MO theory.

Experimental Section

General. ^1H and ^{13}C NMR spectra were recorded on a Bruker WH-90 FT instrument (90 MHz for ^1H) using $CDCl_3$ solutions at room temperature unless indicated otherwise. Chemical shifts (δ) were determined vs. internal Me_4Si. The radical anions were produced by reduction on a potassium mirror at −78 °C in dimethoxyethane and the ESR spectra were registered on a Varian E9 spectrometer. Computer-assisted analysis of the spectra resulted in the ^1H and ^{14}N coupling constants a given below. The assignment of the a_H values of $\mathbf{1}^{-\cdot}$ (R = H) is based on calculations (McLachlan procedure,[21] $\lambda = 1.2$; McConnell relation,[22] $Q = -25.0$ G) and a comparison with the results for $\mathbf{1}^{-\cdot}$ (R = Me). The a_H values agree well with those predicted using the empirical parameters proposed by Gerson et al.[20,23]

The fluorescence spectra were measured on a Spex Fluorolog Model 111C equipped with a multi-alkali R928 photomultiplier tube. Excitation spectra were corrected with the aid of a built-in Rhodamine 6G quantum counter, emission spectra with a calibration curve determined with a standard tungsten lamp. Fluorescence quantum yields were estimated by comparison of the integrated emission intensities with those of a quinine sulfate standard (1 N aqueous H_2SO_4, $\phi_f = 0.55$).[24] A refractive index correction of $n^2(\text{hexane})/n^2\ (H_2SO_4/H_2O) = 1.054$ was applied.

The He(Iα) photoelectron spectra were recorded on a modified Perkin-Elmer PS 16 instrument. The solid samples were inserted directly in the vicinity of the ionization chamber and heated to a temperature of ca. 95 °C (**1**, R = H) and 120 °C (**1**, R = Me). The ionization energies I_v were determined from the peak maxima by in situ calibration with rare gas mixtures.

The nanosecond laser flash photolysis equipment has been described elsewhere.[25] The subnanosecond fluorescence decay measurements used time-correlated single-photon detection after excitation with picosecond mode-locked laser pulses, as described previously.[4] The picosecond transient absorption measurements used excitation by subpicosecond pulses obtained by frequency doubling the amplified output of a colliding-pulse ring dye laser. A continuum probe pulse was obtained by self-phase modulation from the residual fundamental laser pulse. Detection apparatus included a small spectrograph and an optical multichannel analyzer so as to monitor a 180-nm-wide wavelength span on each laser shot. The repetition rate was 10 Hz. Timing information was derived from the position of an optical delay line, using the speed of light as a conversion factor. Further details concerning the construction and performance of the apparatus have been published.[26]

Syntheses. 1,4,7-Triazacycl[3.3.3]azine (1, R = H). Dodecahydro-1,4,7,9b-tetraazaphenalene,[13] formerly a commercial chemical ("Amine-RC 94"), was received as a gift from Shell Chemical Co. and was sublimed (130 °C, 1 Pa) prior to use. The following procedure was found to give slightly better and more reproducible yields than that described previously.[12,13] The saturated amine (9.5 g) was added to a suspension of Pd catalyst on charcoal (2 g, 10% Pd, Fluka) in xylene (0.3 dm^3) and refluxed under an atmosphere of nitrogen. After 2 days the yield of **1** (R = H) had reached a maximum of ca. 4.5% as judged by monitoring the characteristic, structured absorption spectrum in the visible region on an aliquot of the reaction mixture. The solution was filtered and evaporated, and the residual dark oil was triturated with ethyl acetate leaving a colorless precipitate. The violet supernatant was again evaporated and the residue chromatographed with chloroform on neutral aluminum oxide. Evaporation of the purple fraction gave dark crystals of **1** (R = H) which were further purified by repeated fractional sublimation (85 °C, 1 Pa), recrystallization from cyclohexane, and chromatography. The yield of highly pure material was ca. 200 mg (2.3%). A second, very similar purple cyclazine with lower retention on aluminum oxide was obtained in very low yield (ca. 2 mg) but has not been identified. **1** (R = H): dark purple prisms, mp 219–220 °C; ^1H NMR δ 5.41 (d, $J = 6.3$ Hz, C_3-H), 6.87 (d, $J = 6.3$ Hz, C_2-H); ^{13}C NMR δ 111.4 (dd, $J = 174, 8$ Hz, C_3), 154.4 (d, $J = 180$ Hz, C_2), 157.1 ppm (d, $J = \sim 12$ Hz, C_{9a}); mass spectrum, m/e 170.0589 (M^+, 100%, calcd for $C_9H_6N_4$ 170.0592), 143.0480 ($M^+ - HCN$, 10), 85.0284 (M^{2+}, 10); optical spectra (hexane) Figure 1. The first absorption band is quite sensitive to solvent polarity, particularly to the hydrogen bond donating acidity; the first prominent vibrational peak of the S_0–S_1 transition is observed at the following wavelengths: 628 (alkanes), 626 (diethyl ether), 622 (CCl_4 or C_6H_6), 618 ($CHCl_3$), 617 (acetone), 615 (DMF), 613 (CH_3CN), 612 (Me_2SO or CH_3NO_2), 606 (ethanol), 588 nm (H_2O); ESR (radical anion in DME, 213 K) a = 1.372 (N_1), 6.299 (N_{9b}) 5.283 (H_2), 0.305G (H_3).

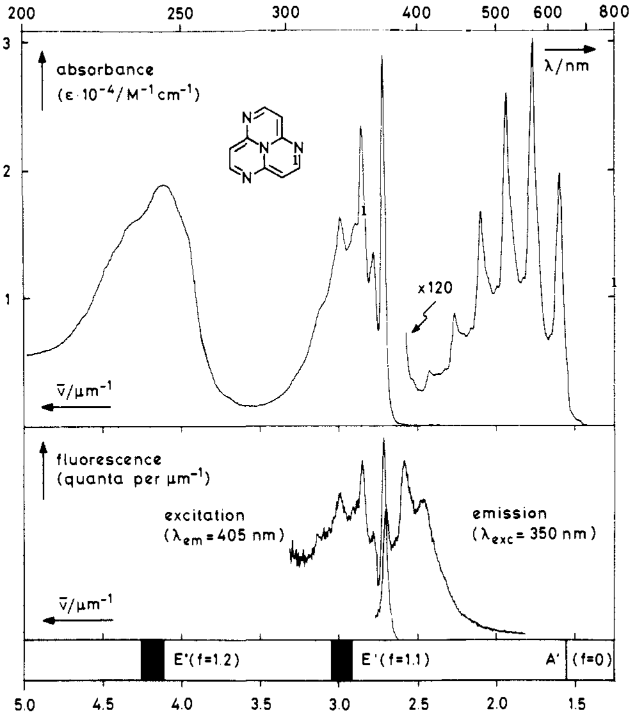

Figure 1. Absorption spectrum (upper half) and corrected fluorescence emission and excitation spectra (lower half) of **1** (R = H) in hexane solution at room temperature. Calculated $\pi\pi^*$ transitions, symmetries (C_{3h} point group), and oscillator strengths f are shown at the bottom.

2,5,8-Trimethyl-1,4,7-triazacycl[3.3.3]azine (1, R = Me). The dehydrogenation of 2,5,8-trimethyldodecahydro-1,4,7,9b-tetrazaphenalene[27] on Pd/C catalyst was reproduced by the method of Mrazek[11] as quoted by Ginzel and Kuffner,[14] yielding 42% of **1** (R = Me) as fine, purple needles: mp 196–197 °C (193–194,[11] 196–197 °C[10]); ^1H NMR δ 1.84 (s, CH_3), 5.43 ppm (s, CH); ^{13}C NMR δ 23.5 (q ($J = 128$ Hz) × d ($J = 3$ Hz), CH_3), 106.9 (q ($J = 4$ Hz) × d ($J = 171$ Hz), C_3), 155.7 (d, $J = 3$ Hz, C_{9a}), 165.4 ppm (q ($J = 6.6$ Hz) × d ($J = 1.5$ Hz), C_2); mass spectrum, m/e 212 (M^+, 100%), 106 (M^{2+}, 6%); the absorption and fluorescence spectra were similar in shape to those of **1** (R = H) shown in Figure 1 with somewhat increased blurring of the vibrational fine structure, emission λ_{max} = 392 nm (ethanol, excitation 365 nm), absorption (pentane, λ_{max} (log ϵ)) 582 (2.26), 532 (2.39), 490 (2.30), 454 (2.09), 426 (1.83), 371 sh (4.04), 365 (4.32), 359 (4.22), 347 (4.31), 333 (4.21), 246 nm (4.39); ESR spectrum (radical anion in DME, 213 K) a = 1.400 (N_1), 5.860 (N_{9b}), 0.154 (H_3), 5.140 G (CH_3).

Results

Optical Spectra. The absorption, fluorescence emission, and fluorescence excitation spectra of **1** (R = H) are shown in Figure 1. The transition energies, oscillator strengths f, and symmetry assignments predicted by standard PPP SCF SCI calculations[28] are displayed as a bar diagram on the bottom of Figure 1. An idealized geometry (C_{3h}, bond lengths 140 pm, bond angles 120°) was assumed for these calculations, all singly excited $\pi\pi^*$ configurations were included, and the standard parameter set was used ($I_{\dot{N}} - I_C = 15.9$, $I_{\ddot{N}} - I_C = 3.5$, $\gamma_C = 10.84$, $\gamma_{\ddot{N}} = 18$, $\gamma_{\dot{N}} = 12.3$, $\gamma_{\mu\nu} = 1439.5/(132.8 + R_{\mu\nu}/\text{pm})$, $\beta_{CN} = \beta_{CC} = -2.318$ eV).

The fluorescence emission spectrum (Figure 1) exhibits an approximate mirror-image relationship to the second absorption

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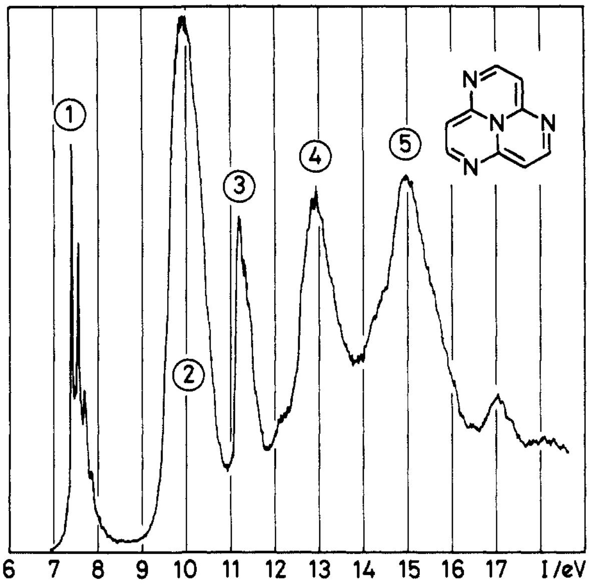

Figure 2. He(Iα) photoelectron spectrum of **1** (R = H).

band of **1** (R = H) and the fluorescence excitation spectrum is, within experimental accuracy, in agreement with the UV absorption of this compound. No fluorescence emission to the red of the first absorption band was observed by using conventional fluorescence instrumentation (Experimental Section). Special care was taken to eliminate the ubiquitous pitfall of strongly luminescent adventitious impurities. Repeated purification of the compound by chromatography, recrystallization, and sublimation did not diminish the intensity of the blue fluorescence emission. Also, prolonged irradiation of the samples did not produce any changes in the emission or excitation spectra. The fluorescence emission must be short-lived ($\tau \lesssim 1$ ns), since degassing or oxygen saturation (1 atm) had no influence on the intensity or spectral shape of the emission.

Similar results were obtained with the trimethyl derivative **1** (R = Me), cf. Experimental Section. Notably, both the first and the second band are shifted hypsochromically by the methyl substituents, $\Delta\tilde{\nu}_{00}(S_1) = 0.14\ \mu m^{-1}$, $\Delta\tilde{\nu}_{00}(S_2) = 0.02\ \mu m^{-1}$; the shift of the first band is much more pronounced such that the energy gap between the first and second excited singlet state is reduced from $\Delta E/hc = 1.30\ \mu m^{-1}$ (**1**, R = H, hexane solution, estimated origin of S_0–S_1 transition, 1.42 μm^{-1}) to 1.18 μm^{-1} (**1**, R = Me, hexane solution, S_0–S_1 transition, 1.56 μm^{-1}). Concomitantly, the S_2 fluorescence yield is reduced from $(5 \pm 1) \times 10^{-4}$ (R = H, $\lambda_{exc} = 350$ nm) to ca. 1×10^{-4} (R = Me, $\lambda_{exc} = 365$ nm).

Compound **1** (R = Me) was also examined using a picosecond excitation pulse $\lambda = 345$ nm, the harmonic of a dye laser pumped by a mode-locked argon ion laser. The lifetime of the blue fluorescence was found to be very short, $\tau_f < 60$ ps. A lifetime on the order of 1 ps is expected from the relation $\tau_f = \phi_f/k_f$, where k_f is estimated by integration of the S_0–S_2 absorption band using the simplified Strickler–Berg equation.[29] In addition, a very weak emission maximum was detected in the red ($\lambda_{max} = 720$ nm, $\tau_f \cong 250$ ps). The red emission was also observed upon excitation at 515 nm ($\tau_f \cong 220$ ps). Thus it is likely that the difference in the lifetimes of the red and blue emissions is significant and that these emissions arise from different excited states. The subnanosecond lifetimes of the two fluorescence features provide further evidence that these emissions are not due to an adventitious contamination by low concentrations of strongly luminescent impurities.

In conclusion, we attribute the blue emissions observed with compounds **1** (R = H and Me) to S_2–S_0 fluorescence. The weak emission of **1** (R = Me) in the red is compatible with S_1–S_0 fluorescence but not with S_2–S_1 fluorescence:[4] the latter is expected to occur at longer wavelengths ($\Delta E/hc = 1.18\ \mu m^{-1}$, $\lambda >$ 850 nm) and should have the same lifetime as the blue emission.

Table I. Vertical Ionization Energies $I_{v,J}$ and Calculated Orbital Energies ϵ_J of **1**

band	$-\epsilon_J$/eV[a] (R = H)	assignment	$I_{v,J}$/eV R = H	$I_{v,J}$/eV R = Me
1	7.38	a″(π)	7.40	7.16
2	9.95, 9.97, 10.37	e″(π), e′(n), a′(n)	10.0 ± 0.4	9.7 ± 0.5
3	11.39	a″(π)	11.20	10.61
4	12.36	e″(π)	12.9	~12.4
5	15.53	a″(π)	15.0 (?)	?

[a] The π-orbital energies were calculated by the PPP SCF method (see text); the valence-state ionization potential of carbon was taken as $I_C = 10$ eV. The n-orbital energies quoted from ref 16 were obtained by an EWMO calculation.

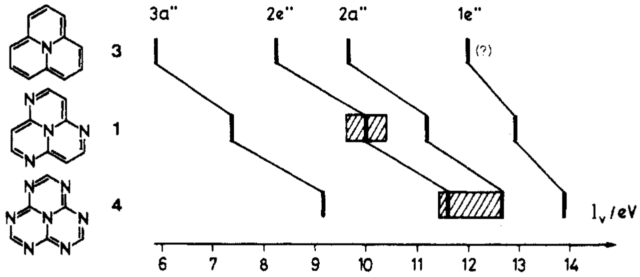

Figure 3. Correlation of the experimental π-ionization energies I_v of compounds **3**,[33] **1**(R = H), and **4**.[6] Symmetry labels refer to the C_{3h} point group. Shaded areas indicate overlap with aza lone pair ionization bands.

He(Iα) Photoelectron Spectra. The PE spectrum of **1** (R = H) is shown in Figure 2; the corresponding vertical ionization energies and the tentative assignments are collected in Table I together with those for **1** (R = Me). Both spectra were of very similar appearance apart from the energy differences noted in Table I. We are aware that these spectra may be deceptively simple, since configuration interaction calculations for the radical cations of **1** (R = H)[30] and of **3**[30,31] indicate extensive mixing of Koopmans' and non-Koopmans' configurations (shake-up configurations) even for the low-lying electronic states. In view of these predicted complications it is perhaps surprising that the following simple-minded correlation procedure (Figure 3), which relies on the validity of Koopmans' theorem, appears to provide satisfactory results.

There is ample evidence that the effect of aza substitution on the π-ionization energies of aromatic compounds is well described by additive, first-order perturbations.[32] Thus the π-bands of **1** (R = H) should lie at the arithmetic means of the corresponding π-ionization energies of the reference compounds **3** and **4**. Relying on the assignments given previously for the PE spectra of the latter compounds,[6,33] we obtain good agreement down to the third π-band. The prediction thus derived for the fourth π-band of **1** (R = H) scores a considerable error of ca. 0.8 eV. The present purely heuristic correlation procedure suggests that the fourth π-band of **3** (symmetry species e″ under the C_{3h} point group) may have to be associated with the strong peak near 12 eV rather than with the weak feature at 10.3 eV.[33] Note that the assignments given in Figure 3 as well as the slopes of the empirical correlation lines agree, within the usual limits of accuracy, with the predictions of closed-shell PPP SCF calculations (cf. Table I).

We conclude that the predicted[30,31] breakdown of single-particle models, i.e., of the application of Koopmans' theorem, for cycl-

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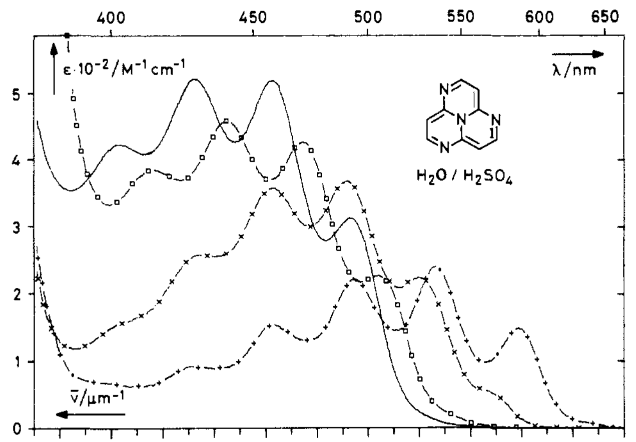


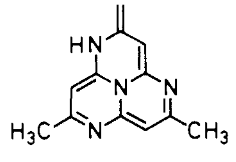
Figure 4. Changes in the visible absorption spectrum of **1** (R = H) in aqueous sulfuric acid solutions due to the successive protonation of the peripheral nitrogen atoms ((+) **1**, pH >6: (×), $\mathbf{1}H^+$, pH 1; (□) $\mathbf{1}H_2^{2+}$, $H_0 = -5.2$; (—) $\mathbf{1}H_3^{3+}$, $H_0 = -9.5$).

[3.3.3]azines is not clearly manifest in the conventional photoelectron spectra of these compounds, unless one resorts to a somewhat ad hoc interpretation of band intensities. Other information, such as the electronic absorption spectra of the corresponding radical cations, will be essential to clarify these questions. At this point, we wish to emphasize that the seemingly convincing correlation procedure (Figure 3) is hampered by the overlapping ionization bands associated with the aza nitrogen lone pairs of compounds **1** and **4**. In the spectra of compounds **1**, these bands (e′ and a′) are lumped together with the second π-band (e″) to the broad, unresolved features appearing in the range of 10.0 ± 0.4 eV (R = H) and 9.7 ± 0.5 eV (R = Me), respectively. An average energy of ca. 10 eV and a splitting of less than 1 eV for these n ionizations are quite consistent with previous results,[6,8,32] with a semiempirical calculation for **1** (R = H, cf. Table I),[16] and with a correlation between lone pair ionization potential averages and the basicity of aza heterocycles (cf. below) reported by Brogli et al.[32]

Protonation Equilibria in Aqueous Sulfuric Acid. Compound **1** (R = H) is readily soluble in water and stable for at least several days both in the presence of base (1 N NaOH) and acid (up to neat H_2SO_4). Due predominantly to hydrogen bonding, the first absorption band is markedly blue-shifted (0.11 μm^{-1}) in neutral or basic aqueous solution relative to alkane solvents (for other solvents see Experimental Section). In increasingly acidic solutions, stepwise color changes from purple-red (H_2O) to orange-red, yellow-orange, and finally yellow (concentrated H_2SO_4) indicate the sequential protonation of the three peripheral nitrogen atoms. Ionization ratios were measured spectrophotometrically and evaluated by the multiwavelength analysis computer program SPECFIT of Zuberbühler and co-workers,[34] using 20–50 monitoring wavelengths in the visible region. The residual standard error was 3×10^{-4} absorbance units for the titration in aqueous solution and 7×10^{-3} for the concentrated sulfuric acid mixtures; the much larger but still moderate error of the latter series arises from the repositioning of the sample cells in the spectrometer after the preparation of each solution and, possibly, from slight but real changes of the individual absorption spectra due to changes in the solvent composition.

The analysis yielded the visible absorption spectra of the four species **1**, $\mathbf{1}H^+$, $\mathbf{1}H_2^{2+}$, and $\mathbf{1}H_3^{3+}$ (R = H, Figure 4) and the three corresponding acidity constants $pK_1 = 3.46$, $pK_2 \cong -2.2$, and $pK_3 \cong -7.2$. The first of these was determined accurately in dilute aqueous solution (10^{-3} M **1** (R = H), initial acid 10^{-2} M CH_3COOH and 10^{-2} M HCl, ionic strength adjusted to 0.1 M with NaCl, 25 ± 0.1 °C, statistical error <0.001 p*K* units). The second and third acidity constants were estimated as half-protonation values on the H_0 scale.[35] The slope of the log ionization ratios did not deviate significantly from unity on the H_0 scale near pK_2 ($m = 0.9 \pm 0.2$) but was somewhat lower ($m = 0.76 \pm 0.05$) near pK_3 in highly concentrated sulfuric acid.

On the basis of the following observations and in agreement with previous work on cyclazines[36-38] all three sites of protonation are located at the peripheral nitrogen atoms. (i) The color changes are entirely reversible and no deuterium incorporation is observed in D_2O/D_2SO_4 solutions, as judged by ^1H NMR. Note, however, that rapid deuteration does occur at the methyl groups of **1** (R = Me) in the presence of either base or acid,[10] presumably via an enamine tautomer of structure **5**. (ii) The absorption spectra of the different species retain their general *habitus* and differ mainly in an increasing hypsochromic shift of the first band with increasing protonation, as expected (cf. Discussion). (iii) The ^1H NMR signals of **1** (R = H) are gradually shifted to lower field in the corresponding D_2O/D_2SO_4 mixtures (all chemical shifts relative to dioxane, δ 3.70): D_2O (**1**) δ 5.65 (d, *J* = 6.5 Hz), 6.97 (d, *J* = 6.6 Hz); D_2SO_4/D_2O ca. 2 wt. % ($\mathbf{1}H^+$) δ 6.09 (d, *J* = 6.8 Hz), 7.36 (d, *J* = Hz); D_2SO_4/D_2O ca.60 wt. % ($\mathbf{1}H_2^{2+}$) δ 6.63 (d, *J* = 7.2 Hz), 7.73 (d, *J* = 7.2 Hz); D_2SO_4 ca. 94 wt % ($\mathbf{1}H_3^{3+}$) δ 6.87 (br d, *J* ~ 6.7 Hz), 7.84 (br d, *J* = 7.3 Hz). Note that the mono- and diprotonated forms appear to retain C_{3h} symmetry due to rapid exchange on the NMR time scale. The symmetry reduction is, however, discernible in the visible absorption spectra of these species (Figure 4) from the increased intensity of the first band, particularly its origin. The overall intensity of this symmetry-forbidden (C_{3h}) transition also shows a general trend to increase from **1** to $\mathbf{1}H_3^{3+}$, presumably due to increasing vibrational intensity borrowing from S_2 with the decreasing S_2–S_1 energy gap.



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Flash Photolysis of 1 (R = H). The Triplet State. No transient absorptions were detected by laser flash photolysis of **1** (R = H) by using laser excitation pulses of ca. 20-ns duration at either 308, 353, or 530 nm. A very weak transient absorption was observed around 390 nm on a subpicosecond laser system: the rise time was below 1 ps and the lifetime ca. 120 ± 50 ps (hexane solution). This transient may be due to absorption from the lowest excited singlet state S_1 of **1** (R = H), compatible with the S_1 fluorescence emission lifetime of **1** (R = Me, ca. 200 ps). There was no evidence for a photochemical decomposition of **1** (R = H).

In order to estimate the excitation energy of the lowest triplet state T_1 of **1** (R = H), we have determined its efficiency as a triplet quencher with a series of benzenoid hydrocarbon sensitizers in degassed benzene solution by flash photolysis. The bimolecular rates of sensitizer quenching by **1** (R = H) were approximately diffusion-controlled (1×10^{10} M^{-1} s^{-1}) for triplet naphthalene (E_T = 255 kJ/mol)[39] and anthracene 178 kJ/mol)[39] and immeasurably slow (<10^5 M^{-1} s^{-1}) for dibenzo[*a,h*]pyrene (144 kJ/mol)[40,41] and tetracene (123 kJ/mol).[39] Dibenzo[*a,i*]pyrene (169 kJ/mol)[40] and perylene (148 kJ/mol)[42] were quenched with a rate of 2 ×

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10^8 and 5×10^5 M^{-1} s^{-1}, respectively. The rapid drop of the quenching rate between 178 and 148 kJ/mol indicates that the quencher **1** (R = H) has very similar geometries in the lowest triplet and singlet ground state[43] and allows us to bracket the adiabatic triplet energy of **1** (R = H) within the range of E_T = (168 ± 5) kJ/mol. This is very close to the energy of the lowest singlet state in benzene solution, E_S = 172 kJ/mol.

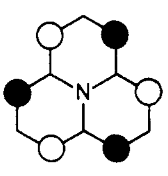
The sensitization of **1** (R = H) did not give rise to any transient absorption in the range 380–400 nm. Indeed, the lifetime of T_1 (**1**, R = H) must be very short, $\tau(T_1) < 1$ μs. This was established by the following experiment: triplet naphthalene was produced by laser excitation at 308 nm in the presence of 1×10^{-4} M **1** (R = H) and 1×10^{-5} M β-carotene ($E_T \cong 96$ kJ/mol).[44] It was found that the decay rate of triplet naphthalene (418 nm) and the rate of formation of triplet carotene (535 nm) were equal within the limits of error, $k = (1.2 \pm 0.1) \times 10^6$ s^{-1}. Thus the sensitization of β-carotene was due only to triplet naphthalene and did not occur via T_1 (**1**, R = H) as a relay.

Discussion

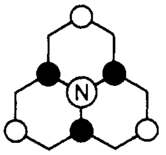
1,4,7-Triazacycl[3.3.3]azine (**1**, R = H) is easily accessible and exhibits several interesting physical and chemical properties. It is soluble and stable in all solvents including water and its color is highly sensitive to solvent and substituent effects. E.g., the sequential protonation of the three peripheral nitrogen atoms in aqueous sulfuric acid is readily observed by color changes (Figure 4) from purple red to orange-red ($pK_1 = 3.46$, $1 \rightleftharpoons 1H^+$), to yellow-orange ($pK_2 \cong -2.2$, $1H^+ \rightleftharpoons 1H_2^{2+}$), and finally to yellow ($pK_2 \cong -7.2$, $1H_2^{2+} \rightleftharpoons 1H_3^{3+}$). Thus compound **1** (R = H) may be useful as an indicator for highly acidic solutions. The central nitrogen atom is completely nonbasic, as in other cyclazines.[36-38] After accounting for the statistical factors on K_1 and K_3, the differences $pK_1 - pK_2$ and $pK_2 - pK_3$ are nearly equal as predicted by Bjerrum's simple electrostatic repulsion model;[45] the ΔpK values of ca. 5 log units are reproduced by assuming a dielectric constant $\epsilon \cong 12$ within the molecule and a charge separation $r(N \cdots N) \cong$ 420 pm.

In general terms, the physical and chemical properties of **1** (R = H) are, as expected, intermediate between the widely different properties of the highly reactive, "antiaromatic"[19] or "biradicaloid"[3] parent cycl[3.3.3]azine (**3**) and the essentially inert hexaaza derivative **4**.[5,6] E.g., the first ionization potential of **1** (R = H; $I_{1,v}$ = 7.40 eV) is very close to the average of $I_{1,v}(3)$ = 5.87 eV[33] and $I_{1,v}(4)$ = 9.16 eV.[6] The same is true for the first absorption band which is shifted through the entire visible range in this series: $\tilde{\nu}_{00}$(**1**, R = H, hexane) = 1.42 μm^{-1}, $\tilde{\nu}_{00}$(**3**, hexane) = 0.78 μm^{-1},[3] $\tilde{\nu}_{00}$(**4**, CH_3CN) = 2.10 μm^{-1}.[7] Qualitatively, these trends are reflected in the chemical properties of **1** (R = Me),[10] **3**,[19] and **4**.[5,6] As a notable exception, both **3** and **4** rapidly react with protic solvents, whereas **1** is stable in aqueous solution. Of course, the hydrolyses of **3** and **4**, respectively, are two entirely different reactions.

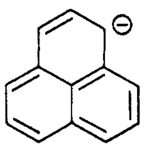
It is illuminating to recast the monotonic changes in the series **3** → **1** → **4** in terms of simple MO perturbation theory. The stabilization of cycl[3.3.3]azine (**3**) by substitution at the peripheral positions 1, 3, etc. with inductive charge acceptors, which had provided the key to the original synthesis of **3** by Leaver and co-workers,[19] is a striking example of the "topological charge stabilization" concept recently popularized by Gimarc:[46] "... nature prefers to place atoms of greater electronegativity in those positions where the topology of the structure and electron-filling level tend to pile up extra charge in the isoelectronic hydrocarbon". Phenalenyl anion (**6**⁻), the reference system for compounds **1**, **3**, and **4**, is an alternant, odd hydrocarbon; therefore its excess charge distribution is simply equal to the square of the nonbonding HOMO.[47] Note that in contrast to expectations based on resonance theory, the central bridging atom carries no excess charge. This explains why nitrogen substitution at the center of the molecule (**6**⁻ → **3**) yields a highly reactive compound, as pointed out some time ago by Dewar and Trinajstic.[48] It also explains why further aza substitution at the peripheral positions 1, 3, etc. (**3** → **1** → **4**) is accompanied by an impressive decrease in the chemical reactivity, particularly toward oxidizing agents.[3,46]



HOMO



LUMO



6⁻

The frontier orbitals of **3** (HOMO and LUMO) can be immediately derived without any calculation by considering the interaction of the p-AO on the central atom with the two nonbonding MO's of the 12π perimeter.[3] Note that the frontier orbitals are localized to mutually exclusive regions of the molecule. The spatial separation of these orbitals is manifested in the spin density distributions of the radical ions $3^{+\cdot}$, $3^{-\cdot}$,[20] and $1^{-\cdot}$. Thus S_0–S_1 excitation (HOMO → LUMO) is accompanied by a profound redistribution of charge and indeed the position of the first absorption band is very sensitive to inductive perturbation. An increase in the electronegativity at positions 1, 3, etc. (C → N or N → NH^+) will essentially stabilize only the HOMO and thus give rise to a blue shift of the S_0–S_1 band. This explains the regular shifts with increasing protonation of **1** (R = H; cf. Figure 4) and the sensitivity to solvent polarity, particularly to the hydrogen bond donating strength of the solvent. Conversely, the methyl substituents in positions 2, 5, and 8 (**1**, R = Me) will essentially destabilize only the LUMO and again give rise to a blue shift. This result is unusual, since alkyl substitution of aromatic compounds normally leads to a bathochromic shift of the absorption bands. A related, well-documented exception is found in azulenes substituted at positions 1 and 5.[49] Finally, the three benzo groups in tricycloquinazoline (**2**) will tend to split the originally degenerate, nonbonding MO's of the 12π perimeter and thus the S_0–S_1 transition is again blue-shifted; trisdehydro[12]annulene provides a similar case.[50]

The photophysical properties of **1** (R = H) are quite unusual but reasonably well understood. We have observed a weak fluorescence emission from the second ππ* excited singlet state S_2 (E′ symmetry, cf. Figure 1) on a conventional fluorescence spectrometer, whereas emission from the symmetry-forbidden (A′) S_1 state was barely detectable by pulsed-laser excitation. Thus compound **1** (R = H) represents a borderline case between parent cycl[3.3.3]azine (**3**), which emits only from S_2 in violation of Kasha's rule,[3,4] and tri-s-triazine (**4**), which shows normal S_1 fluorescence.[7] Qualitatively, this trend may be attributed to the dramatic shift of the S_1 band in the series **3**, **1**, **4**, which is accompanied by a decrease in the S_2–S_1 energy gap, $\Delta E(3)/hc$ = 1.40 μm^{-1},[3] $\Delta E(1, R = H)/hc$ = 1.30 μm^{-1}, and $\Delta E(4)/hc$ = 1.18

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μm^{-1}.[7] It should nevertheless be noted that the radiationless decay rate of S_2 (**1**, R = H), $k_{nr} \cong 2 \times 10^{11}$ s^{-1}, calculated from $\phi_f = (5 \pm 1) \times 10^{-4}$ and $k_f \cong 1 \times 10^8$ s^{-1}, is over 2 orders of magnitude larger than that predicted from an energy gap relation empirically parametrized for polyacenes.[51] Inasmuch as this correlation may be considered valid for the heterocycles **3**[4] and **1**, this discrepancy may be taken as an indication for the presence of an additional $n\pi^*$ state(s) between the $\pi\pi^*$ states S_1 and "S_2". Not surprisingly, the protonated forms of **1** exhibit normal S_1 fluorescence only, since the S_2–S_1 energy gap is further reduced upon protonation. E.g., a solution of **1**H$^+$ (R = Me) in 0.1 N aqueous sulfuric acid gave rise to a red emission (λ_{max} = 620 nm, $\phi_f = 5 \times 10^{-4}$) with a lifetime of $\tau_f = 0.6 \pm 0.1$ ns.

Another unusual feature is the near degeneracy of the lowest $\pi\pi^*$ singlet and triplet states of **1** (R = H), $|E(S_1) - E(T_1)| <$ 10 kJ/mol, and the short lifetime of the latter, $\tau(T_1, 300\ K) <$ 1 μs. The small singlet–triplet energy gap is a further manifestation of the frontier-orbital separation in space; a detailed discussion was given previously.[3] The short lifetime of T_1 is tentatively attributed to a rapid radiationless deactivation via $T_1 \rightarrow S_1$ intersystem crossing. Thus the unusual sequence of the excited-state energies of **1** (R = H), $E(S_2) >> E(S_1) \cong E(T_1)$, appears to result in a very rapid and efficient radiationless deactivation of this molecule after electronic excitation or triplet sensitization. As a consequence, **1** (R = H) is quite stable to photochemical decomposition.

Our tentative assignments of the ionization bands of compounds **1** (R = H and Me) as given in Table I are consistent with the previous assignments for **3** (a reassignment of the fourth π-band 1e″ is proposed, Figure 3)[33] and **4**[6] which were based on semiempirical and ab initio (STO-3G) calculations. However, we emphasize that both the previous calculations[6,33] and the present simple correlation procedure rely on the applicability of Koopmans' theorem. Such a procedure appears to be highly questionable in view of PPP CI calculations for **1** and **3** which predict that a simple one-to-one correspondence between ionization bands and canonical bonding orbitals does not exist for this type of compound.[30,31] Thus a more detailed investigation, including, e.g., the electronic absorption spectra of the corresponding radical cations, may well lead to a revision of some or all of the spectral assignments beyond bands 1 in this series of compounds.[52]

Acknowledgment. This work is part of Project 2.213-0.84 of the Swiss National Science Foundation. The picosecond laser studies were supported in part by the NSF. Financial support was received from Ciba-Geigy SA, Hoffmann-La Roche SA, Sandoz SA, and the Ciba-Stiftung. We are most grateful to Prof. F. Gerson and Dr. G. Plattner, Basel, for the ESR spectra of $1^{-\cdot}$ (R = H, Me), Prof. A. Zuberbühler, Basel, for the multiwavelength analysis[34] of the protonation equilibria, and Shell Chemical Co. for a generous gift of "Amine-RC-94".

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Some Aspects of the Electronic Hypersurface of Bis(methylene)phosphorane. An Experimental and Theoretical Approach

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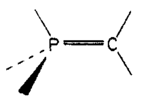
Abstract: Bis(methylene)phosphoranes possess a strongly polarized π-system, isoelectronic to the allyl anion. Jahn–Teller distortion of the electronic ground-state hypersurface causes weak pyramidalization at phosphorus. Its magnitude depends on the substituents. The electrocyclic ring-closure reaction to phosphacyclopropane is conrotatory. Electron-accepting substituents (e.g., silyl groups) at the carbon atoms stabilize the open bis(methylene)phosphorane and disfavor the ring-closure reaction. The electrochemical investigations are in support of the theoretical analysis. The redox reactions are irreversible. While the CV oxidation peaks are independent of the substituents on bis(methylene)phosphorane, the reduction peak potentials considerably increase with NR_2 or OR at phosphorus.

Coordination at phosphorus decreases in the order of structures **1**–**3**. From a historical point of view, the first member in this



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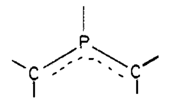

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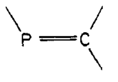

3

series, methylenephosphorane (**1**), has gained much attention, from experimental[1] as well as theoretical[2] investigators. In comparison, only recently the first synthesis and structural elucidation of

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