segregated hydrocarbon and polar regions, a relatively dry hydrocarbon core, and significant water contact only at the core interface. Micellar chains are highly disordered, a point on which there is general agreement, and chain bending can place double bond segments part of the time at or near the interface where they will be exposed to water. If reaction occurs during that time it can take on some of the characteristics of an aqueous or polar process and thus give misleading information about the overall exposure of the hydrocarbon to water. A process such as segment protrusion accounts for apparent polar micellar reactivities without having to propose significant water penetration into the micelle.

Acknowledgment. The continued support of NSERC Canada is gratefully acknowledged. R.B.L. thanks the Government of Ontario and NSERC for the provision of fellowships.

Registry No. CTAB, 57-09-0; CTAC, 112-02-7; SDS, 151-21-3; Brij-35, 9002-92-0; (*Z*)-6-octadecenoic acid, 593-39-5; (*Z*)-6-octadecen-1-ol, 2774-87-0; (*Z*)-9-octadecenoic acid, 112-80-1; (*Z*)-9-octadecen-1-ol, 143-28-2; methyl (*Z*)-9-octadecenoate, 112-62-9; (*E*)-9-octadecenoic acid, 112-79-8; (*E*)-9-octadecen-1-ol, 506-42-3; (*E*)-11-octadecenoic acid, 693-72-1; (*Z*)-13-docosenoic acid, 112-86-7; (*Z*)-13-docosen-1-ol, 629-98-1; methyl (*Z*)-13-docosenoate, 1120-34-9; (*E*)-13-docosenoic acid, 506-33-2; (*Z*)-15-tetracosenoic acid, 506-37-6; [(*R*)-(*E*)]-12-hydroxy-9-octadecenoic acid, 540-12-5; (*Z*,*Z*)-9,12-octadecadienoic acid, 60-33-3; (*Z*,*Z*,*Z*)-9,12,15-octadecatrienoic acid, 463-40-1; 1-monooleoyl-*rac*-glycerol, 30836-40-9; dioleoylglycerol, 25637-84-7; 1,2,3-trioleoylglycerol, 122-32-7; dimethyl (*E*)-13-hexacosendioate, 102072-63-9.

A N–N Three-Electron σ Bond. Structure of the Radical Cation of *N*,*N'*-Trimethylene-*syn*-1,6:8,13-diimino[14]annulene as Studied by ESR Spectroscopy and X-ray Crystallographic Analysis

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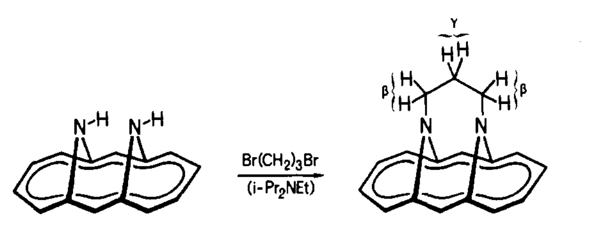
Contribution from the Institut für Physikalische Chemie and Institut für Anorganische Chemie der Universität Basel, 4056 Basel, Switzerland, and Institut für Organische Chemie der Universität, D-5000 Köln 41, West Germany. *Received December 13, 1985*

Abstract: *N*,*N'*-Trimethylene-*syn*-1,6:8,13-diimino[14]annulene (**2**), synthesized from the parent diimino[14]annulene (**1**), is easily oxidized in solution to its radical cation $\mathbf{2}^{\bullet+}$ ($E_{1/2}$ = +0.24 V vs. SCE). The high thermodynamic and kinetic stability as well as the large ^{14}N hyperfine coupling constant (1.685 mT) strongly suggest that $\mathbf{2}^{\bullet+}$ is a N-centered radical cation with a N–N three-electron σ bond formed upon oxidation of **2**. This structure is fully confirmed by an X-ray analysis carried out on the red-brown crystals of $\mathbf{2}^{\bullet+}ClO_4^-$. A substantial decrease in the N–N interatomic distance from 2.705 Å in **2** to 2.160 Å in $\mathbf{2}^{\bullet+}$ is associated with a flattening of the 14-membered perimeter.

Reaction of *syn*-1,6:8,13-diimino[14]annulene (**1**)[2] with 1,3-dibromopropane in the presence of *N*-ethyldiisopropylamine (150 °C, 48 h) affords the *N*,*N'*-trimethylene derivative **2**[3] in moderate yield. Bearing a close structural relationship to 1,5-diazabicyclo[3.3.3]undecane,[4] a medium-ring bicyclic diamine, the compound **2** should be subject to interesting chemical transformations not only at the peripheral annulene ring but also at the N–(CH$_2$)$_3$–N bridging group.



1 **2**

The cyclic voltammogram of **2** exhibits a reversible oxidation wave at +0.24 V (vs. SCE), as compared to +0.78 V for an irreversible wave of **1**.[5] Accordingly, **2** is easily oxidized to a thermodynamically stable radical cation $\mathbf{2}^{\bullet+}$ by a variety of agents such as Pb^{4+}, NO$^+$, Ag$^+$, and tris(*p*-bromophenyl)amminium cation. The kinetic stability (persistence) of $\mathbf{2}^{\bullet+}$ depends sensitively on the nature of the counterion; under favorable conditions (exclusion of air, with ClO_4^- as the counterion), the half-life of $\mathbf{2}^{\bullet+}$ in solution is of the order of weeks.[6]

Figure 1 shows the ESR spectrum of $\mathbf{2}^{\bullet+}$ observed at 298 K upon reaction of **2** with the $SbCl_5^-$ salt of the amminium cation in dichloromethane (g = 2.0036 ± 0.0001). Because of the trimethylene chain undergoing conformational interconversion at a rate (k) comparable to the hyperfine time scale ($\sim 10^7$ s^{-1}), several groups of lines in the spectrum are broadened beyond detection;[7] they appear in the fast exchange limit ($k > 5 \times 10^8$ s^{-1}) attained above 400 K.[8] Although poor solubility of the salts of $\mathbf{2}^{\bullet+}$ at temperatures lower than 250 K makes ESR studies in the slow exchange limit ($k < 10^6$ s^{-1}) experimentally inaccessible, an activation barrier, E_a, of 6.8 ± 0.9 kcal/mol (28 ± 4 kJ/mol) could be derived for the interconversion process.[9] Analysis of

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(1) (a) Physikalische Chemie, Basel. (b) Organische Chemie, Köln. (c) Anorganische Chemie, Basel.

(2) Vogel, E.; Kuebart, F.; Marco, J. A.; Andree, R.; Günther, H.; Aydin, R. *J. Am. Chem. Soc.* **1983**, *105*, 6982.

(3) Characterization of **2**: reddish-brown crystals (from ether), mp 154–155 °C; ^{1}H NMR (300 MHz, CD$_2$Cl$_2$) δ 0.19 (quint., 2 H), 1.24 (t, 4 H), 7.42 and 7.76 (AA'BB', 8 H), 9.09 (s, 2 H); ^{13}C NMR (75 MHz, CD$_2$Cl$_2$) δ 22.70, 50.31, 118.89, 128.98, 133.49, 140.95; MS (70 eV) m/z 248 (M$^+$, 100), 220 (53), 206 (27), 191 (28), 178 (26); IR (CsI) 3037, 1514 cm^{-1}; UV–vis (MeOH) λ_{max} = 295 nm (ϵ = 144000), 372 (7600), 438 (1100) (sh), 572 (480). Andree, R. Dissertation, Universität Köln, 1985. Vogel, E.; Andree, R.; Marco, J. A.; Zeng, X., to be published.

(4) Alder, R. W.; Sessions, R. B. In *The Chemistry of Amino, Nitroso, and Nitro Compounds and their Derivatives*; Patai, S., Ed.; Wiley: Chichester, 1982; p 763. Alder, R. W. *Acc. Chem. Res.* **1983**, *16*, 321.

(5) Working electrode, platinum disk; counter electrode, glassy carbon; solvent, acetonitrile; supporting salt, Et$_4$NBF$_4$; temperature, 298 K; voltage scan, 200 mV/s.

(6) UV–vis spectrum of $\mathbf{2}^{\bullet+}ClO_4^-$ (MeOH): λ_{max} = 295 nm (ϵ = 92000), 356 (4500), 375 (4700), 445 (500), 500 (550), 518 (530) (sh), 590 (ca. 50) (sh).

(7) For a closely analogous example see: Gerson, F., *High-Resolution ESR Spectroscopy*; Wiley: New York; Verlag-Chemie: Weinheim, 1970; Chapter A.2.3.

(8) Knöbel, J. Dissertation, Universität Basel, 1985.

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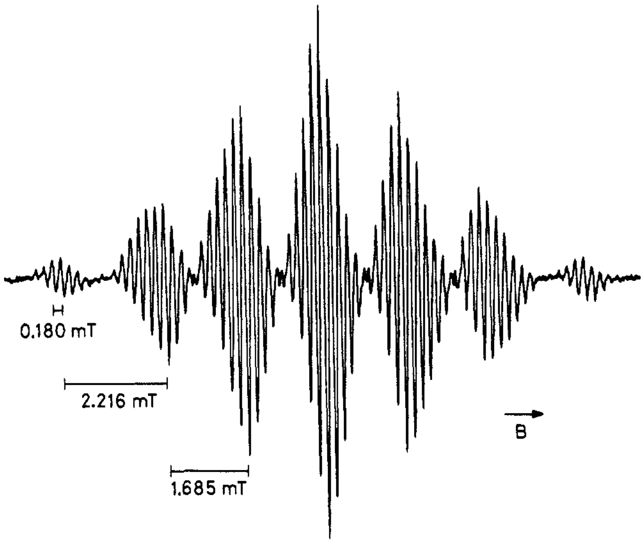
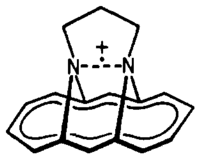


Figure 1. ESR spectrum of $2^{\bullet+}$. Solvent, H_2CCl_2; counterion, $SbCl_6^-$; temperature, 298 K.

the hyperfine pattern yields two large coupling constants: 1.685 ± 0.015 mT for the two ^{14}N nuclei and 1.108 ± 0.010 mT for the four protons in the two methylene groups adjacent to the N atoms (β protons). The latter (exchange averaged) value is equal to half the splitting of 2.216 ± 0.020 mT observable at 298 K (Figure 1). An additional smaller coupling constant of 0.180 ± 0.005 mT, due to eight protons, has tentatively been assigned to six (out of ten) perimeter protons and to the two protons in the single methylene group not neighboring the N atoms (γ protons). The high thermodynamic and kinetic stability, as well as the size of the ^{14}N- and β-proton coupling constants, which is unusually large for a π-radical cation extending over 14 C atoms, strongly suggest that $2^{\bullet+}$ is a N-centered paramagnetic species with a N–N three-electron σ bond.[4] As will be demonstrated below, such a structure is in full accord with an X-ray crystallographic analysis of $2^{\bullet+}$.



$2^{\bullet+}$

The X-ray study has been performed on red-brown needles of $2^{\bullet+}ClO_4^-$ (150° C dec) obtained upon reaction of 2 with $AgClO_4$ in dichloromethane and subsequent recrystallizations from a 7:1 mixture (per volume) of tetrahydrofuran with nitromethane. Crystal data for $2^{\bullet+}ClO_4^-$: $C_{17}H_{16}ClN_2O_4$, $M = 347.78$, monoclinic, space group $P2_1/c$, $a = 8.695$ (3) Å, $b = 18.707$ (3) Å, $c = 9.717$ (3) Å, $\beta = 95.14$ (3)°, $Z = 4$, $D_c = 1.467$ g cm^{-3}, $D_o = 1.46$ g cm^{-3}, μ(Mo Kα) = 2.19 cm^{-1}. The structure was solved by direct methods and by difference Fourier techniques and it was refined by blocked-matrix least squares to $R = 0.0906$ ($R_w = 0.0841$; $w = [\sigma^2(2F_o) + 0.00690(F_o)^2]^{-1}$, using 1526 reflections with $F > 3\sigma(F)$ (no correction for absorbance). Intensity data, collected on an Enraf-Nonius CAD4 diffractometer in the range $2 < \theta < 26°$, were corrected for anisotropic decay with time (maximum decay correction was 1.62).

Figure 2 reproduces an Ortep plot of the radical cation $2^{\bullet+}$. Table I lists the average values of bond lengths, bond angles, and torsion angles,[10] together with the analogous X-ray data for the neutral molecule 2.[11] The most remarkable change on passing from 2 to $2^{\bullet+}$ is the decrease in the N–N interatomic distance from 2.705 to 2.160 Å, which indicates an onset of a bonding interaction between the two N atoms. The N–N bond length in $2^{\bullet+}$ (2.160 Å) agrees excellently with the theoretical values, 2.16[12] and 2.164 Å,[13] calculated for $H_3N{-}{-}{-}NH_3^{\bullet+}$. To our knowledge, a direct observation of a N–N three-electron σ bond has only very recently

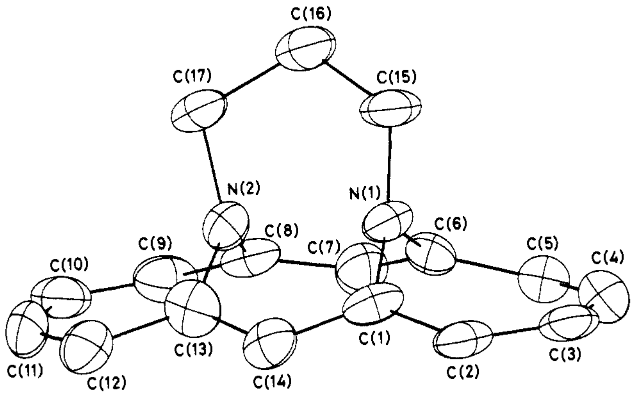
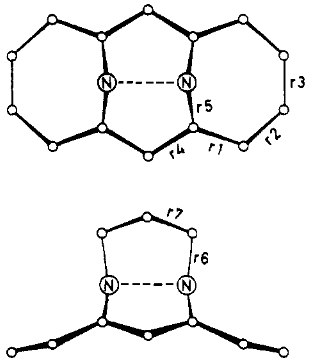


Figure 2. Ortep projection of $2^{\bullet+}$. The numbering of the atoms is the same as previously used for 2.[11]

Table I. Average Geometry of $2^{\cdot+}$, as Compared to That of 2



	$2^{\cdot+}$	2
	Bond Lengths,[a] Å	
r1	1.401	1.408
r2	1.389	1.372
r3	1.376	1.396
r4	1.404	1.393
r5	1.414	1.406
r6	1.498	1.452
r7	1.539	1.494
N–N	2.160	(2.705)
	Bond Angles,[b] deg	
r1r2	123.3	123.9
r2r3	129.3	128.5
r1r4	127.8	123.4
r4r4	118.2	125.1
r1r5	116.4	114.0
r4r5	115.7	121.8
r5r5	115.8	112.7
r5r6	120.8	122.8
r6r7	107.3	115.2
r7r7	106.8	115.4
	Torsion Angles,[c] deg	
$\phi 1$	159.6	150.3
$\phi 2$	18.7	18.6
$\phi 4$	171.6	157.9

[a] Uncorrected values for both 2 and $2^{\cdot+}$. [b] Sides of the angle are given. [c] ϕj is torsion angle across the rj bond.

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(9) A method for calculation of E_a under these conditions is described in the following: Gerson, F.; Ohya-Nishiguchi, H.; Plattner, G. *Helv. Chim. Acta* **1982**, *65*, 551.

(10) The standard deviations of the individual bond lengths and bond angles in $2^{\cdot+}$ are 0.009–0.015 Å and 0.7–0.9°, respectively.

(11) Destro, R.; Pilati, T.; Simonetta, M.; Vogel, E. *J. Am. Chem. Soc.* **1985**, *107*, 3192.

(12) See footnote 10 in the following: Alder, R. W.; Sessions, R. B. *J. Am. Chem. Soc.* **1979**, *101*, 3651.

(13) Bouma, W. J.; Radom, L. *J. Am. Chem. Soc.* **1985**, *107*, 345.

been reported for the radical cation of 1,6-diazabicyclo[4.4.4]-tetradecane (**3**).[14] Although the N–N bond length in $\mathbf{3}^{\bullet+}$ (2.295 Å) is markedly larger than in $\mathbf{2}^{\bullet+}$, the shortening in the N–N interatomic distance on going from **3** to $\mathbf{3}^{\bullet+}$ (2.806 - 2.295 Å = 0.511 Å)[14] is comparable to that found in the present work for $\mathbf{2}^{\bullet+}$ relative to **2** (2.705 - 2.160 Å = 0.545 Å). On the other hand, the average C–N–C angle in $\mathbf{2}^{\bullet+}$ is $(1/3)(2 \times 120.8° + 115.8°) = 119.1°$, as against the corresponding value of 114.0° in $\mathbf{3}^{\bullet+}$.[14] The N atoms in $\mathbf{2}^{\bullet+}$ should therefore be approximately sp^2 hybridized with the N–N bond having an almost pure p character, whereas a hybridization intermediate between sp^2 and sp^3 is expected for the N atoms in $\mathbf{3}^{\bullet+}$ with a considerable s contribution to the N–N bond. This difference accounts for the far larger ^{14}N-coupling constant for $\mathbf{3}^{\bullet+}$ (3.59 mT)[15] than for $\mathbf{2}^{\bullet+}$ (1.685 mT) and may also be of interest in considering the N–N bond lengths.

The mean C–C bond length, 1.395 Å, and the mean C–C–C bond angle, 125.6°, along the 14-membered perimeter in $\mathbf{2}^{\bullet+}$ are not significantly different from the corresponding values for **2** (1.392 Å and 125.2°). It is evident from Table I that the apparent constancy of the mean bond length is due to compensation of changes which alternate in sign along the perimeter. One is tempted to trace back these changes to the nodal properties of the HOMO by considering the lengthening (shortening) of a bond upon ionization as a consequence of the removed bonding (antibonding) contribution of the lost electron.

An increase in the torsion angles $\phi 1$ and $\phi 4$ for $\mathbf{2}^{\bullet+}$ relative to **2** indicates a flattening of the perimeter brought about by a decrease in the N–N distance. Similar findings are reported in the series of the structurally related hydrocarbons.[16] Thus, the perimeter is flattened when the two bridging C atoms in *syn*-1,6:8,13-propane-1,3-diylidene[14]annulene are linked by a bond to yield the corresponding cyclopropanediylidene-bridged compound. The decrease in the N–N distance also gives rise to substantial changes in the geometry parameters of the N–$(CH_2)_3$–N bridging group: on passing from **2** to $\mathbf{2}^{\bullet+}$, the bond lengths become larger and the bond angles smaller.

Acknowledgment. This work was supported by the Swiss National Science Foundation (F. Gerson) and the Stiftung Volkswagenwerk (E. Vogel). We thank Mr. D. Becker, (Universität Köln) for preparing a batch of **2**.

Supplementary Material Available: Tables listing (i) fractional coordinates, (ii) details of data collection and structure refinements, (iii) structure factors F_o/F_c, and (iv) individual bond lengths and bond angles (15 pages). Ordering information is given on any current masthead page.

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Photochemistry of Phenyl Azide: The Role of Singlet and Triplet Phenylnitrene as Transient Intermediates

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Abstract: The sequence of transient intermediates formed by the photolysis of phenyl azide (**1**) was determined by a combination of techniques including absorption, emission, and EPR spectroscopies as well as quantitative product analyses of irradiated glassy solutions at 77 K, in addition to kinetic and spectrographic flash photolysis at various temperatures. Several ortho, ortho′-disubstituted derivatives of **1** were also studied. The prevailing reaction pathway of **1** at ambient temperature is different from that at 77 K. The change of mechanism is traced to a temperature-dependent branching ratio from the primary photoproduct, singlet phenylnitrene (^{1}**2**). It is established that the photoproduct observed by absorption spectroscopy at 77 K is predominantly triplet phenylnitrene (^{3}**2**), as was originally postulated by Reiser et al. (*Trans. Faraday Soc.* **1966**, *62*, 3162–3169).

The chemical reactions initiated by the elimination of molecular nitrogen from aryl azides have found many useful applications in heterocyclic syntheses, in the production of photoimaging devices, and in the biochemical method of photoaffinity labeling.[1] Despite extensive work performed on the parent system, phenyl azide (**1**), essential aspects of the reaction mechanism remain controversial, and the literature concerning phenylnitrene (**2**) as the key reactive intermediate is as abundant as it is confusing.[1-14] Part of the complexity undoubtedly originates in the wide diversity of the reaction conditions employed, which range from gas-phase pyrolysis at temperatures up to 1000 K[2] to pyrolysis and photolysis in solution to photolysis of rigid glassy solutions at 77 K and of inert gas matrices at 10 K. We propose that the competition between two decay processes of singlet phenylnitrene (^{1}**2**), the thermally activated isomerization to 1-azacyclohepta-1,2,4,6-tetraene (**3**) and the temperature-insensitive intersystem crossing

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