Formal Transfers of Hydride from Carbon−Hydrogen Bonds. Generation of H_2 from Orthoformamides Designed To Undergo Intramolecular Protonolyses of Activated Carbon−Hydrogen Bonds

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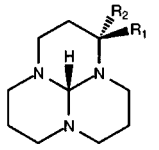
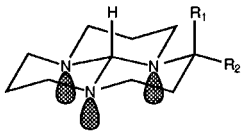
Protonolysis of the central carbon−hydrogen bond of tricyclic orthoformamide **1** occurs readily to liberate H_2 and give the corresponding guanidinium ion **15** under mild conditions. To accelerate this process, we have attempted to make the reaction intramolecular by constructing molecules in which carbon−hydrogen bonds similarly activated as formal donors of hydride are held close to acidic sites. Spectroscopic and structural studies have indicated that orthoformamide **25** contains a central carbon−hydrogen bond activated as a formal donor of hydride by three antiperiplanar lone pairs on nitrogen, as well as an acidic ethylammonium group. As expected, pyrolysis of compound **25** produced the corresponding guanidinium ion **28** in high yield, and H_2 was liberated and could be trapped in 39% yield. However, analogous bimolecular reactions of butylammonium chloride with simple orthoformamides **1** and **29**, which do not contain intramolecular acidic sites, occurred at similar rates. This suggests that protonolyses of such structures may occur by collinear attack on the activated central carbon−hydrogen bond or that the observed liberation of H_2 does not involve direct protonolysis.

Introduction

Carbon−hydrogen bonds serve as formal donors of hydride in a variety of well-known redox reactions.[2] Of particular practical importance are reactions of this type that occur during catalytic cracking and reforming, as well as closely related reactions in which protonolyses of the carbon−hydrogen bonds of simple alkanes by strong acids produce carbocations and H_2.[3] To learn more about these fundamental yet poorly understood processes, we have made a series of compounds that incorporate carbon−hydrogen bonds designed to be especially good formal donors of hydride,[4,5] and we have studied their reactions with acids. This work has shown that tricyclic orthoformamide **1** is a particularly suitable substrate for protonolysis, and its activated central carbon−hydrogen bond reacts with acids to liberate H_2 and give the corresponding guanidinium ion under surprisingly mild conditions.[4,6] Our work has suggested that the remarkable reactivity of compound **1** is a stereoelectronic consequence of its preference for conformation **1a**, which weakens and polarizes the central carbon−hydrogen bond by placing it antiperiplanar to three lone pairs on nitrogen.[4,7]





1 (R_1 = R_2 = H)
5 (R_1 = CN, R_2 = H)
6 (R_1 = CH_2NH_2, R_2 = H)
7 (R_1 = $CH_2NH_3^+$, R_2 = H)
8 (R_1 = H, R_2 = CH_2NH_2)
11 (R_1 = H, R_2 = CN)
13 (R_1 = H, R_2 = $CH_2NH_3^+$)

1a (R_1 = R_2 = H)
5a (R_1 = CN, R_2 = H)
8a (R_1 = H, R_2 = CH_2NH_2)

To further accelerate protonolyses of carbon−hydrogen bonds, we have attempted to make the process intramolecular by constructing molecules in which carbon−hydrogen bonds activated as formal donors of hydride are held close to acidic sites.[8] The unusual reactivity of orthoformamide **1** suggests that especially promising candidates for intramolecular protonolyses of carbon−hydrogen bonds can be represented by general structure **2**, in which the hydridic central carbon−hydrogen bond of a tricyclic orthoformamide is held close to an ap-

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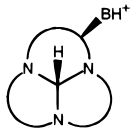

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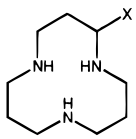


3 (X = H)
4 (X = CN)

propriately oriented acidic site BH^+ created by protonating conjugate base B. In this paper, we describe the synthesis, structure, and reactions of compounds that incorporate these novel features. We find that compounds of this type do indeed liberate H_2, but our results suggest that the process does not occur by direct intramolecular protonolysis of the central carbon−hydrogen bond.

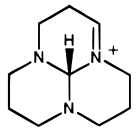
Results and Discussion

Tricyclic orthoformamide **1** can be prepared by condensing 1,5,9-triazacyclododecane (**3**) with formamidinium salts, so we expected to be able to make precursors of target **2** by analogous condensations of carbon-substituted derivatives of triazacycloalkanes. Unfortunately, normal condensation of 1,5,9-triazacyclododecane-2-carbonitrile (**4**)[9] with formamidinium acetate gave the desired cyanoorthoformamide **5** in very low yield. After extensive study, however, we found that compound **5** could be prepared in 42% yield by conducting the condensation in the presence of a large excess of KCN. We suggest that α-cyanoamine **4** exists in equilibrium with the imine resulting from loss of HCN and that the role of excess KCN is to displace this equilibrium, thereby minimizing secondary reactions involving the imine.[10]

Careful spectroscopic analysis provided unambiguous evidence that orthoformamide **5** favors conformation **5a**. In particular, a strongly shielded singlet at δ 2.81 in the ^{1}H NMR spectrum ($CDCl_3$) and the presence of a series of Bohlmann bands in the region 2690−2500 cm^{-1} in the IR spectrum ($CHCl_3$) indicated that the central carbon−hydrogen bond must be antiperiplanar to three lone pairs.[4,11] In addition, we could establish by ^{13}C NMR spectroscopy that the three-bond coupling constants $^3J_{CH}$ between the cyano carbon atom and the hydrogen atoms of the adjacent methylene group are distinctly different (2.5 Hz and 12.2 Hz), which requires that the cyano group must be axial. Similar stereoelectronic preferences for antiperiplanar orientations of cyano groups and lone pairs in α-cyanoamines have been noted previously.[12] As a result, the stereochemical and conformational preferences of compound **5** are all predictable features that are consistent with clear precedents and with direct spectroscopic evidence.

By design, these preferences create a molecule with a central carbon−hydrogen bond strongly activated as a formal source of hydride, in close proximity to an axial cyano group that can be converted into a site suitable for protonation. In particular, we were optimistic that reduction would yield axial (aminomethyl)orthoformamide **6** and that subsequent protonation of the primary amine would yield a salt **7** capable of undergoing intramolecular protonolysis. In fact, however, reduction with $LiAlH_4$ produced the unexpected equatorial stereoisomer **8**, which was isolated in 77% yield. Analysis of the ^{1}H NMR spectrum ($CDCl_3$) revealed a singlet at δ 2.63 for the central methine hydrogen and a multiplet at δ 2.16 for the other methine hydrogen. These characteristically shielded signals indicated that the central methine carbon−hydrogen bond must again be antiperiplanar to three lone pairs and that the other methine carbon−hydrogen bond must be axial and antiperiplanar to a single lone pair. As a result, the aminomethyl group must be equatorial, and structure **8a** can be assigned to the preferred conformation. In this structure, the axial central carbon−hydrogen bond is suitably activated as a formal donor of hydride, but the equatorial basic site is oriented in a way that would prevent its conjugate acid from participating in an intramolecular protonolysis.

In principle, formation of the unexpected equatorial amine **8** could result from the following steps: reversible elimination of cyanide from orthoformamide **5** to give tricyclic iminium ion **9**, bicyclic formamidinium ion **10**, or a structure intermediate between these two limiting forms;[4,13] readdition of cyanide to form small amounts of



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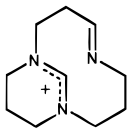

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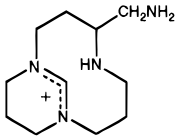

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stereoisomeric orthoformamide **11**; and kinetically favorable reduction of the equatorial cyano group to give equatorial amine **8**.[10] However, the following two observations are inconsistent with this mechanism for the formation of compound **8**: (1) Trapping of iminium ion **9**, isomeric formamidinium ion **10**, or an intermediary structure by $LiAlH_4$ would be expected to generate characteristic side products such as orthoformamide **1**, which was not observed,[14] and (2) only 22% exchange occurred when a solution containing orthoformamide **5** (0.033 M) and excess $K^{13}CN$ (0.27 M) in DMSO was kept at 25 °C for 16 days. This demonstrates that the cyano group is labile, but it suggests that formation of isomeric cyanoorthoformamide **11** by ionization would be too slow to account for the stereochemical results of reduction. Instead, we suggest that the desired axial amine **6** may

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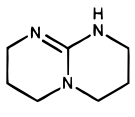
be the kinetic product of reduction, but it then isomerizes to the thermodynamically more stable equatorial isomer **8**, presumably by an acid-catalyzed process that produces bicyclic formamidinium ion **12** or an isomeric structure as an intermediate. The axial and equatorial hydrogen atoms in preferred conformer **1a** of orthoformamide **1** are known to undergo exchange by an analogous mechanism.[4] It is also possible that axial cyanoorthoformamide **5** is converted reversibly by a similar process into small amounts of its equatorial isomer **11**, which is then reduced preferentially to give equatorial (aminomethyl)-orthoformamide **8**. The stereochemistry of its conjugate acid **13** is not suitable for intramolecular protonolysis; fortunately, however, the intermediate formation of bicyclic formamidinium ion **12** or an isomeric structure may offer a potentially rapid mechanism for isomerizing equatorial ammonium ion **13** to the desired axial isomer **7**, thereby permitting intramolecular protonolysis.

To study this possibility, we needed to prepare adequate amounts of (aminomethyl)orthoformamide **8**. Because its synthesis from 1,5,9-triazacyclododecane is an expensive and tedious 10-step procedure, we attempted to devise a more direct method. Deprotonation of the commercially available guanidine **14**, followed by alkylation with 1,3-dibromopropane, is known to produce tricyclic guanidinium ion **15**, which can then be reduced



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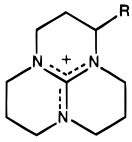
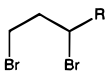
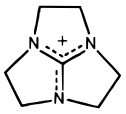


15 (R = H)
16 (R = CN)



17 (R = CN)
18 (R = $CONH_2$)

to orthoformamide **1**.[15] We were optimistic that an analogous alkylation of guanidine **14** with 2,4-dibromobutanenitrile (**17**) would yield the corresponding cyanoguanidinium ion **16** directly and ultimately provide a very convenient route to the required (aminomethyl)-orthoformamide **8**. Dehydration of the known 2,4-dibromobutanamide (**18**)[16] by P_2O_5 gave nitrile **17** in 62% yield.[17] We then found that compound **17** does indeed react with guanidine **14** to form a tricyclic guanidinium ion, but the initial step in this reaction is base-induced elimination of HBr from nitrile **17** to give (*E*/*Z*)-γ-bromocrotononitrile, and the final product is not the expected guanidinium ion **16**. We obtained similar results when we prepared (*E*/*Z*)-γ-bromocrotononitrile by the standard method[18] and used it in place of dibromonitrile **17**. Spectroscopic analysis of the bromide salt of the product revealed signals at δ 116.0 and 151.7 in the ^{13}C NMR spectrum ($CDCl_3$) characteristic of a cyano group and the central carbon atom of a guanidinium ion; in addition, a peak diagnostic of a cyano group appeared at 2247 cm^{-1} in the IR spectrum (KBr) of the corresponding tetrafluoroborate salt, as well as two bands at 1593 and 1672 cm^{-1} corresponding to stretching modes of an unsymmetric guanidinium ion. In comparison, the tetrafluoroborate salts of symmetric tricyclic guanidinium ions **15** and **19** have stretching bands at 1590 and 1655 cm^{-1}, respectively,[4] and the perchlorate salt of unsymmetric guanidinium ion **20** shows two peaks at 1597 and 1684 cm^{-1}.[19] For these reasons, we were forced to conclude that the product of the reaction of guanidine **14** with (*E*/*Z*)-γ-bromocrotononitrile is not guanidinium ion **16** but rather the unexpected isomer **21**, which was isolated in 80% yield as its bromide salt. This compound presumably results from initial alkylation, followed by an intramolecular Michael addition.[20]



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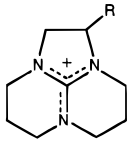
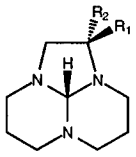
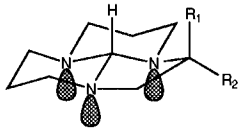


20 (R = H)
21 (R = CH_2CN)
24 (R = $CH_2CH_2NH_3^+$)

Subsequent reduction of the bromide salt of guanidinium ion **21** with $NaBH_4$ gave a 67% yield of an orthoformamide assigned structure **22**. Detailed analysis of its NMR and IR spectra indicated that conformation **22a** is adopted in solution. In particular, the presence of a Bohlmann band at 2461 cm^{-1} ($CHCl_3$) provided evidence that the central carbon−hydrogen bond is antiperiplanar to three lone pairs. This conclusion is supported by the highly shielded chemical shift (δ 2.19) of the central methine hydrogen atom in the ^1H NMR spectrum ($CDCl_3$). In addition, the other methine hydrogen atom is coupled to two adjacent endocyclic methylene hydrogens with constants $^3J_{HH}$ of 9.1 and 3.2 Hz. This methine hydrogen must be pseudoaxial because the larger coupling constant involves the methylene hydrogen that is more shielded and must itself be antiperiplanar to a lone pair. As a result, the cyanomethyl group must be pseudoequatorial. To confirm these conclusions, we determined the structure of orthoformamide **22** by X-ray crystallography, and the results are shown in Figure 1. The structure demonstrates conclusively that orthoformamides **1** and **22** both incorporate central carbon−hydrogen bonds activated as formal donors of hydride by three antiperiplanar lone pairs.



22 (R_1 = H, R_2 = CH_2CN)
23 (R_1 = H, R_2 = $CH_2CH_2NH_2$)
25 (R_1 = H, R_2 = $CH_2CH_2NH_3^+Cl^-$)
27 (R_1 = $CH_2CH_2NH_3^+Cl^-$, R_2 = H)
29 (R_1 = H, R_2 = H)



22a (R_1 = H, R_2 = CH_2CN)
23a (R_1 = H, R_2 = $CH_2CH_2NH_2$)
25a (R_1 = H, R_2 = $CH_2CH_2NH_3^+Cl^-$)

(15) Alder, R. W.; Mowlam, R. W.; Vachon, D. J.; Weisman, G. R. *J. Chem. Soc., Chem. Commun.* **1992**, 507.
(16) Ikuta, H.; Shirota, H.; Kobayashi, S.; Yamagishi, Y.; Yamada, K.; Yamatsu, I.; Katayama, K. *J. Med. Chem.* **1987**, *30*, 1995.
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(18) Couvreur, P.; Bruylants, A. *Bull. Soc. Chim. Belg.* **1952**, *61*, 253.
(19) Mowlam, R. W. Ph.D. Thesis, University of Bristol, 1990.
(20) For a similar observation, see: Selby, T. P.; Smith, B. K. *J. Heterocycl. Chem.* **1989**, *26*, 1237.

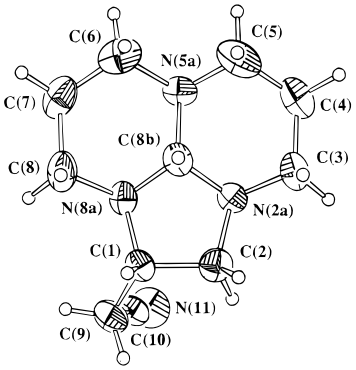
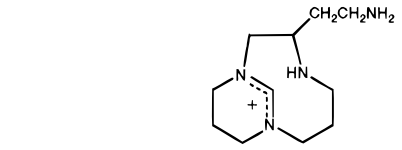


Figure 1. ORTEP drawing of the structure of (cyanomethyl)orthoformamide **22**. Hydrogen atoms appear as spheres of arbitrary size, and other atoms are represented by ellipsoids corresponding to 40% probability.

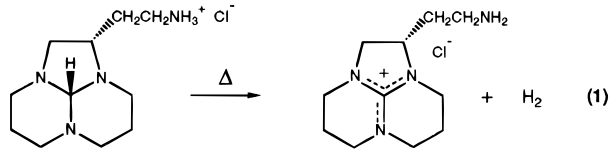
As a result, we expected orthoformamide **22** to be an effective reducing agent and an active substrate for protonolyses. Moreover, its synthesis is very simple, so we decided to use compound **22** in further studies of intramolecular protonolysis in place of the less accessible isomer **5**. Reduction of compound **22** with $LiAlH_4$ in CH_2Cl_2 provided the expected aminoethyl derivative **23** in quantitative yield. The presence of a characteristically shielded singlet at δ 2.01 in the ^1H NMR spectrum ($CDCl_3$) and a Bohlmann band at 2446 cm^{-1} in the IR spectrum ($CHCl_3$) indicated that the central carbon−hydrogen bond of compound **23** is antiperiplanar to three lone pairs and that conformation **23a** is presumably favored. Oxidation with $Hg(OOCCH_3)_2$ at 25 °C occurred rapidly and gave the diacetate salt of tricyclic guanidinium ion **24** in 89% yield. The presence of two bands at 1593 and 1674 cm^{-1} in the IR spectrum ($CHCl_3$) demonstrated that guanidinium ion **24** retains the five- and six-membered rings of orthoformamide **23** and that there is no skeletal rearrangement involving the exocyclic aminoethyl group. The corresponding dichloride salt was obtained in quantitative yield from the diacetate by metathesis using excess methanolic HCl.

Protonation of (aminoethyl)orthoformamide **23** with gaseous HCl in dry CH_2Cl_2 provided the expected ammonium chloride **25** in quantitative yield. The ^1H NMR spectra of orthoformamide **23** and its salt **25** proved to be generally similar, except that the methylene hydrogen atoms α to the NH_3^+ group in salt **25** are conspicuously deshielded. The singlet characteristic of the central methine hydrogen appears in salt **25** at δ 2.16 ($CDCl_3$), only 0.15 ppm downfield of the corresponding singlet in the spectrum of free base **23**. Similar features appear in ^1H NMR spectra recorded in D_2O. Together, these observations confirm that protonation occurs on the primary amino group, as expected, and that the product is a tricyclic orthoformamide rather than bicyclic formamidinium ion **26** or a related structure. Furthermore, replacement of the acidic ammonium hydrogens in salt **25** by deuterium yielded a derivative with a broad N−D stretching band centered at 2179 cm^{-1} in the IR spectrum ($CHCl_3$). The similarity of this band to that of $CH_3(CH_2)_3ND_3^+Cl^-$ and the concentration independence of its position indicated that in $CHCl_3$ there is no intramolecular N−H···N hydrogen bond involving the orthoformamide nitrogen atoms in chloride **25**. Its preferred conformation, assigned structure **25a**, must therefore be closely similar to that of free base **23**. This structure incorporates a central carbon−hydrogen bond activated as a formal donor of hydride by three antiperiplanar lone pairs, but the acidic site is held in an orientation that does not permit intramolecular protonolysis. Nevertheless, the behavior of orthoformamide **1** and related compounds made us optimistic that thermolysis of salt **25** under conditions of acid catalysis would allow reversible opening to give intermediate bicyclic formamidinium ion **26** or a related structure, thereby permitting equilibration with axial ethylammonium salt **27** and subsequent formation of H_2 by intramolecular protonolysis.

As expected, thermolysis of salt **25** produced significant amounts of H_2. The products of thermolysis were determined in the following way. One arm of an H-tube was charged with solid salt **25** and the other with a suspension of Pd/C in a stirred ethanolic solution of *trans*-stilbene. The tube was sealed under N_2, and the arm containing the salt was heated at 145 °C for 44 h. Under these conditions, H_2 was evolved and was trapped as 1,2-diphenylethane in 39% yield. Acidification of the residual pyrolysate with methanolic HCl provided the dichloride salt of guanidinium ion **24**, which was isolated in 82% yield. These observations confirmed that thermolysis of salt **25** causes protonolysis of the central carbon−hydrogen bond as expected, thereby liberating H_2 and generating the corresponding guanidium chloride **28** (eq 1).



26

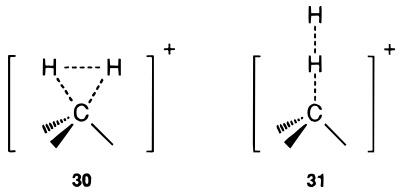


25 **28**

Similar thermolyses could also be effected in a variety of solvents. Unexpectedly, however, the following experiments indicated that thermolysis of salt **25** does not occur by direct intramolecular protonolysis in the manner for which the compound was originally devised. Heating a 0.40 M solution of salt **25** in DMSO-d_6 at 120 °C for 68 h in a sealed tube produced guanidinium chloride **28** in 90% yield, while a control experiment demonstrated that heating a solution containing equimolar amounts of unsubstituted orthoformamide **29** (0.40 M)[15] and butylammonium chloride (0.40 M) in DMSO-d_6 under identical conditions generated the chloride salt of the corresponding guanidinium ion **20** at a similar rate. In addition, unsubstituted orthoformamide **1** showed comparable behavior when heated with butylammonium chloride. These observations indicated that the presence of the acidic ethylammonium group in orthoformamide **25** does not lead to accelerated protonolysis of the central carbon−hydrogen bond.

Conclusions

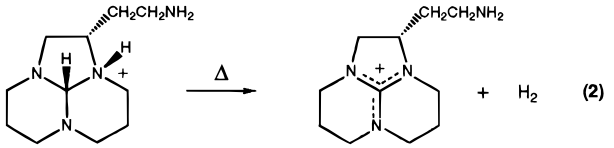
There are two limiting trajectories for the protonolysis of a carbon−hydrogen bond: an orthogonal approach produces triangular structure **30**, whereas a collinear approach yields structure **31**.[3b] Structure **30** is normally



30 **31**

considered to be favored because it results from an electronically stabilizing interaction of a proton with a filled σ_{CH} orbital; in addition, intermediate formation of structure **30** readily accounts for the hydrogen−deuterium exchange that is known to occur when alkanes are treated with strong deuterated acids.[3] Such exchange does not occur during the protonolysis of orthoformamide **1**,[4] so it is possible that steric factors associated with the unique tricyclic skeleton of compound **1** favor alternative structure **31**. If so, intramolecular protonolysis may not be accelerated in derivatives of orthoformamide **1** that have been designed to permit orthogonal protonation of the activated central carbon−hydrogen bond by a nearby acidic site.

Alternatively, the evolution of H_2 that occurs when orthoformamide **1** and related compounds are treated with acids may involve processes other than direct protonolysis of the activated central carbon−hydrogen bond. For example, heating salt **25** may promote reversible transfer of a proton to one of the less basic orthoformamide nitrogen atoms, thereby leading to bicyclic formamidinium ion **26**, tricyclic ammonium ion **32**, an intermediary structure,[13] or one of their many regio- and stereoisomers. Structure **32** and its isomers may then undergo a formally forbidden but strongly exothermic[21] syn elimination of H_2 (eq 2). This mechanism offers an



32 **28** (2)

attractive explanation for the failure of salt **25** to evolve H_2 more readily than simpler tricyclic orthoformamides in which intramolecular protonolysis is impossible.

Experimental Section

Ether and tetrahydrofuran (THF) were dried by distillation from the sodium ketyl of benzophenone, CH_2Cl_2 was dried by distillation from CaH_2, and HCl was dried by passage over concentrated H_2SO_4. Other commercial reagents were used without further purification.

(1*RS*,9b*SR*)-Hexahydro-1*H*,4*H*,7*H*,9b*H*-3a,6a,9a-triazaphenalene-1-carbonitrile (5). A solution of the tris(trifluoroacetate) salt of 1,5,9-triazacyclododecane-2-carbonitrile (**4**; 264 mg, 0.490 mmol),[9] formamidinium acetate (204 mg, 1.96 mmol), and KCN (321 mg, 4.93 mmol) in deoxygenated absolute C_2H_5OH (10 mL) was stirred at 25 °C for 22 h under a slow current of N_2. Volatiles were then removed by evaporation under reduced pressure, and the residue was partitioned between CH_2Cl_2 and 10% aqueous KOH. The aqueous phase was extracted with CH_2Cl_2, and the combined organic phases were dried over anhydrous Na_2SO_4 and decolorized with activated carbon. Evaporation of solvent under reduced pressure left a residue that was purified by sublimation (50 °C/10^{-5} Torr) to give (1*RS*,9b*SR*)-hexahydro-1*H*,4*H*,7*H*,9b*H*-3a,6a,9a-triazaphenalene-1-carbonitrile (**5**; 42.0 mg, 0.204 mmol, 42%) as a colorless solid. Recrystallization from hexane provided an analytically pure sample: mp 123−124 °C; IR ($CHCl_3$) 2824, 2772, 2689, 2527 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.46 (ddddd, ^2J = 12.8 Hz, ^3J = 2.7, 2.7, 2.7, 2.7 Hz, 1H, H_{5e}), 1.52 (ddddd, ^2J = 12.8 Hz, ^3J = 3.1, 2.6 , 2.6, 2.6 Hz, 1H, H_{8e}), 1.77 (dddd, ^2J = 13.1 Hz, ^3J = 2.6, 2.6, 2.3 Hz, 1H, H_{2e}), 1.96−2.13 (m, 2H, H_{5a} and H_{8a}), 2.18−2.32 (m, 3H, H_{4a}, H_{6a}, and H_{7a}), 2.35 (dddd, ^2J = 13.1 Hz, ^3J = 12.5, 4.3, 4.3 Hz, 1H, H_{2a}), 2.57 (ddd, ^2J = 12.5 Hz, ^3J = 12.5, 2.6 Hz, 1H, H_{3a}), 2.64 (ddd, ^2J = 12.0 Hz, ^3J = 12.0, 3.1 Hz, 1H, H_{9a}), 2.81 (s, 1H, H_{9b}), 2.74−2.85 (m, 5H, H_{3e}, H_{4e}, H_{6e}, H_{7e}, and H_{9e}), 3.87 (dd, ^3J = 4.3, 2.3 Hz, 1H, H_{1e}); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 23.8 (C_8), 24.0 (C_5), 27.0 (C_2), 49.2 (C_3), 51.7 (C_9), 53.1 (C_4, C_6, or C_7), 53.4 (C_4, C_6, or C_7), 53.4 (C_1), 53.7 (C_4, C_6, or C_7), 94.8 (C_{9b}), 116.4 (C_{10}); MS (EI) *m*/*e* 206, 205, 178; HRMS (EI) calcd for $C_{11}H_{18}N_4$ 206.1531, found 206.1516. Anal. Calcd for $C_{11}H_{18}N_4$: C, 64.05; H, 8.79. Found: C, 64.04; H, 8.84.

(1*RS*,9b*SR*)-Hexahydro-1*H*,4*H*,7*H*,9b*H*-3a,6a,9a-triazaphenylene-1-methylamine (8). A suspension of $LiAlH_4$ (19 mg, 0.50 mmol) in dry ether (2 mL) was stirred at 0 °C under dry N_2 and treated with a solution of (1*RS*,9b*SR*)-hexahydro-1*H*,4*H*,7*H*,9b*H*-3a,6a,9a-triazaphenalene-1-carbonitrile (**5**; 34.3 mg, 0.166 mmol) in dry ether (4 mL). The mixture was kept at 25 °C for 22 h, cooled to 0 °C, and treated with 5% aqueous NaOH. After dilution with H_2O, the mixture was extracted with CH_2Cl_2, and the combined extracts were dried with anhydrous Na_2SO_4. Evaporation of solvent under reduced pressure left a residue of pure (1*RS*,9b*SR*)-hexahydro-1*H*,4*H*,7*H*,9b*H*-3a,6a,9a-triazaphenylene-1-methylamine (**8**; 26.8 mg, 0.127 mmol, 77%) as a yellow oil: ^1H NMR (300 MHz, $CDCl_3$) δ 1.30−1.59 (m, 3H), 1.86−2.32 (m, 9H), 2.57 (dd, ^2J = 13.7 Hz, ^3J = 3.0 Hz, 1H), 2.63 (s, 1H), 2.78−3.01 (m, 5H), 3.08−3.15 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 23.3, 24.3, 26.6, 43.9, 46.7, 52.4, 53.3, 53.8, 54.3, 62.0, 98.6; MS (EI) *m*/*e* 210, 209, 180.

2,4-Dibromobutanamide. 2,4-Dibromobutanamide was prepared by the published method[16] and purified in the following way. The crude product was warmed at 50 °C for 2d *in vacuo* (0.1 Torr) and was then sublimed (85 °C/0.1 Torr) to give a colorless solid (51%). Recrystallization from ether provided an analytically pure sample: mp 82 °C; IR ($CHCl_3$) 3516, 3403, 1693 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 2.48 (ddt, ^2J = 15.2 Hz, ^3J = 9.0, 5.4 Hz, 1H), 2.68 (dddd, ^2J = 15.2 Hz, ^3J = 8.3, 6.4, 4.8 Hz, 1H), 3.52−3.65 (m, 2H), 4.55 (dd, ^3J = 9.0, 4.8 Hz, 1H), 6.09 (bs, 1H), 6.31 (bs, 1H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 30.2, 37.5, 47.1, 170.7; MS (EI) *m*/*e* 244; HRMS (EI) calcd for $C_4H_7{}^{79}Br_2NO$ 243.8972, found 243.8952.

2,4-Dibromobutanenitrile (17). An intimate mixture of 2,4-dibromobutanamide (11.4 g, 46.5 mmol) and P_2O_5 (8.87 g, 62.5 mmol) was prepared in a mortar and heated at 180 °C for 10 min under dry Ar in an apparatus equipped for distillation. The apparatus was then evacuated, and the product was distilled into a flask cooled at −78 °C. Redistillation in a Kugelrohr apparatus in the presence of P_2O_5 (100 mg, 0.705 mmol) gave 2,4-dibromobutanenitrile (**17**; 6.51 g, 28.7 mmol, 62%) as a colorless liquid: IR ($CHCl_3$) 2247 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 2.56−2.64 (m, 2H), 3.55−3.59 (m, 2H), 4.59 (dd, ^3J = 7.9, 6.6 Hz, 1H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 25.3, 28.3, 38.5, 116.5.

1-(Cyanomethyl)hexahydro-1*H*,3*H*,6*H*-5a,8a-diaza-2a-azoniaacenaphthylene Bromide (21). A solution of 1,3,4,6,7,8-hexahydro-2*H*-pyrimido[1,2-*a*]pyrimidine (**14**; 5.00 g, 35.9 mmol) in dry deoxygenated THF (83 mL) was stirred at 0 °C under dry N_2 and treated dropwise with a solution of an *E*/*Z* mixture of 4-bromo-2-butenenitrile (11.6 g, 79.5 mmol)[18] in THF (53 mL). The mixture rapidly became deep blue,[22] with a significant amount of precipitate. Deoxygenated 20% aqueous NaOH (39 mL) was added at 0 °C at a rate of 4 mL/h, and stirring was continued at 0 °C for 12 h. The pH was then

(21) Analogous thermal eliminations of H_2 from cyclic alkenes are well-known processes. For references, see: Agrafiotis, D. K.; Rzepa, H. S. *J. Chem. Soc., Perkin Trans. 2* **1989**, 367.

(22) The intense blue color is presumably due to the anion formed by deprotonating (*E*/*Z*)-γ-bromocrotononitrile. For a similar observation, see: Fevig, T. L.; Katzenellenbogen, J. A. *J. Org. Chem*. **1987**, *52*, 247.

adjusted to 7 by the addition of 48% aqueous HBr (15 mL), and volatiles were removed by evaporation *in vacuo* at 25 °C. The residue was triturated with CH_2Cl_2, redried, reduced to a powder, and thoroughly extracted with CH_2Cl_2. Solvent was removed from the combined extracts by evaporation under reduced pressure. H_2O was added to the residue, and the mixture was extracted with CH_2Cl_2. The aqueous phase was filtered, solvent was removed by evaporation *in vacuo*, and the residue was dried at 65 °C/0.1 Torr to give 1-(cyanomethyl)-hexahydro-1*H*,3*H*,6*H*-5a,8a-diaza-2a-azoniaacenaphthylene bromide (**21**; 8.20 g, 28.8 mmol, 80%) as a viscous yellow oil that was used without further purification: ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.12−2.20 (m, 4H), 3.10 (dd, ^2J = 17.4 Hz, ^3J = 4.6 Hz, 1H), 3.22 (dd, ^2J = 17.4 Hz, ^3J = 5.4 Hz, 1H), 3.30−3.63 (m, 9H), 4.10 (dd, ^2J = 9.7 Hz, ^3J = 9.7 Hz, 1H), 4.52−4.57 (m, 1H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 19.6, 19.9, 20.4, 36.6, 40.9, 44.2, 44.2, 51.1, 53.9, 116.0, 151.7; MS (FAB) *m/e* 205, 178, 164.

The corresponding tetrafluoroborate salt was prepared by treating an aqueous solution of the bromide with $NaBF_4$. The solution was then extracted thoroughly with CH_2Cl_2, the combined organic extracts were dried over anhydrous Na_2SO_4, and solvent was removed by evaporation under reduced pressure to leave a residue of the tetrafluoroborate: IR (KBr) 2247, 1672, 1593 cm^{-1}.

(1*RS*,8b*SR*)-(Hexahydro-1*H*,3*H*,6*H*,8b*H*-2a,5a,8a-triazaacenaphthylen-1-yl)acetonitrile (22). A solution of 1-(cyanomethyl)hexahydro-1*H*,3*H*,6*H*-5a,8a-diaza-2a-azoniaacenaphthylene bromide (**21**; 8.20 g, 28.8 mmol) in a mixture of C_2H_5OH (250 mL) and H_2O (150 mL) was stirred at −40 °C and treated with small portions of $NaBH_4$ (6.5 g, 170 mmol). The cooling bath was removed, and the mixture was stirred at 25 °C for 2 d. Volatiles were partially removed by evaporation under reduced pressure. The concentrate was extracted with CH_2Cl_2, the combined extracts were dried with anhydrous Na_2SO_4, and the solvent was removed by evaporation under reduced pressure. The residue was distilled in a Kugelrohr apparatus (110 °C/0.2 Torr), and the distillate was crystallized from hexane to give (1*RS*,8b*SR*)-(hexahydro-1*H*,3*H*,6*H*,8b*H*-2a,5a,8a-triazaacenaphthylen-1-yl)acetonitrile (**22**; 3.99 g, 19.3 mmol, 67%) as colorless needles: mp 98−99 °C; IR ($CHCl_3$) 2813, 2753, 2461, 2251 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.53−1.59 (m, 2H, H_{4e} and H_{7e}), 1.83−1.90 (m, 2H, H_{5a} and H_{6a}), 1.94−2.05 (m, 2H, H_{4a} and H_{7a}), 2.10 (ddd, ^2J = 11.6 Hz, ^3J = 10.2, 2.7 Hz, 1H, H_{3a}), 2.19 (s, 1H, H_{8b}), 2.30 (ddd, ^2J = 11.7 Hz, ^3J = 10.4, 2.8 Hz, 1H, H_{8a}), 2.51 (dd, ^2J = 16.6 Hz, ^3J = 7.5 Hz, 1H, H_9), 2.60 (dd, ^2J = 16.6 Hz, ^3J = 7.5 Hz, 1H, $H_{9'}$), 2.62 (dd, ^2J = 9.2 Hz, ^3J = 9.1 Hz, 1H, H_{2a}), 2.85−2.92 (m, 3H, H_{1a}, H_{5e}, and H_{6e}), 2.95 (dd, ^2J = 9.2 Hz, ^3J = 3.2 Hz, 1H, H_{2e}), 3.02 (dt, ^2J = 10.2 Hz, ^3J = 3.2 Hz, 1H, H_{3e}), 3.21 (ddd, ^2J = 10.4 Hz, ^3J = 4.3, 1.5 Hz, 1H, H_{8e}); ^{13}C NMR (100 MHz, $CDCl_3$) δ 22.8 (C_9), 24.1 (C_4 or C_7), 24.4 (C_7 or C_4), 48.0 (C_8), 49.0 (C_3), 49.9 (C_5 or C_6), 51.3 (C_6 or C_5), 54.2 (C_2), 55.1 (C_1), 98.6 (C_{8b}), 117.8 (C_{10}); MS (EI) *m/e* 206, 205, 164; HRMS (EI) calcd for $C_{11}H_{18}N_4$ 206.1531, found 206.1508. Anal. Calcd for $C_{11}H_{18}N_4$: C, 64.05; H, 8.79; N, 27.16. Found: C, 64.16; H, 8.52; N, 27.09.

(1*RS*,8b*SR*)-2-(Hexahydro-1*H*,3*H*,6*H*,8b*H*-2a,5a,8a-triazaacenaphthylen-1-yl)ethylamine (23). A solution of (1*RS*,8b*SR*)-(hexahydro-1*H*,3*H*,6*H*,8b*H*-2a,5a,8a-triazaacenaphthylen-1-yl)acetonitrile (**22**; 500 mg, 2.4 mmol) in dry CH_2Cl_2 (250 mL) was stirred at −20 °C under dry N_2 and treated with $LiAlH_4$ (375 mg, 9.9 mmol). The cooling bath was removed, and the mixture was heated at reflux for 40 h. The mixture was cooled to 0 °C, treated with 5% aqueous NaOH (5 mL), stirred for 3 h, treated with Na_2SO_4, and filtered. Evaporation of solvent under reduced pressure left a residue of pure (1*RS*,8b*SR*)-2-(hexahydro-1*H*,3*H*,6*H*,8b*H*-2a,5a,8a-triazaacenaphthylen-1-yl)ethylamine (**23**; 510 mg, 2.4 mmol, 100%) as a colorless oil: IR ($CHCl_3$) 2793, 2751, 2446 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.41−1.50 (m, 2H), 1.52−1.70 (m, 2H), 1.72−1.84 (m, 2H), 1.84−2.10 (m, 4H), 2.01 (s, 1H), 2.35−2.50 (m, 2H), 2.60−2.75 (m, 2H), 2.76−2.86 (m, 3H), 2.89−2.96 (m, 1H), 2.99−3.06 (m, 1H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 24.3, 24.3, 36.5, 38.6, 48.3, 49.2, 51.2, 51.5, 54.1, 57.3, 99.0; MS (EI) *m/e* 210, 209; HRMS (EI) calcd for $C_{11}H_{22}N_4$−H 209.1766, found 209.1756.

2-(Hexahydro-1*H*,3*H*,6*H*-5a,8a-diaza-2a-azoniaacenaphthylen-1-yl)ethylammonium Diacetate (24). A solution of (1*RS*,8b*SR*)-2-(hexahydro-1*H*,3*H*,6*H*,8b*H*-2a,5a,8a-triazaacenaphthylen-1-yl)ethylamine (**23**; 95 mg, 0.45 mmol) in absolute C_2H_5OH (5mL) was stirred at 25 °C and treated with a solution of $Hg(OOCCH_3)_2$ (290 mg, 0.91 mmol) in absolute C_2H_5OH (19 mL). After 30 min, the mixture was filtered, and H_2S was bubbled through the filtrate to precipitate salts of mercury. The resulting suspension was filtered, and the filtrate was decolorized with activated carbon. Volatiles were removed by evaporation under reduced pressure to give 2-(hexahydro-1*H*,3*H*,6*H*-5a,8a-diaza-2a-azoniaacenaphthylen-1-yl)ethylammonium diacetate (**24**; 130 mg, 0.40 mmol, 89%) as a colorless oil: IR ($CHCl_3$) 3396, 1674, 1593 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.77 (s, 6H), 1.78−1.85 (m, 1H), 1.93−1.98 (m, 4H), 2.12−2.20 (m, 1H), 2.81 (t, ^3J = 7.3 Hz, 2H), 3.10−3.18 (m, 7H), 3.23−3.27 (m, 2H), 3.66 (t, ^3J = 9.4 Hz, 1H), 3.91−3.97 (m, 1H), 11.14 (bs, 3H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 20.2, 20.4, 22.5, 28.4, 34.6, 39.4, 41.3, 44.6, 44.7, 51.4, 55.8, 151.8, 175.7; MS (FAB) *m/e* 209.

2-Hexahydro-1*H*,3*H*,6*H*-5a,8a-diaza-2a-azoniaacenaphthylen-1-yl)ethylammonium Dichloride (24). A solution of 2-(hexahydro-1*H*,3*H*,6*H*-5a,8a-diaza-2a-azoniaacenaphthylen-1-yl)ethylammonium diacetate (**24**; 117 mg, 0.356 mmol) in CH_3OH (5 mL) was treated at 25 °C with a saturated solution of HCl in CH_3OH, and volatiles were removed by evaporation *in vacuo*. The residue was redissolved in CH_3OH and treated again with HCl in CH_3OH. Removal of volatiles by evaporation under reduced pressure left a residue of 2-hexahydro-1*H*,3*H*,6*H*-5a,8a-diaza-2a-azoniaacenaphthylen-1-yl)ethylammonium dichloride (**24**; 100 mg, 0.356 mmol, 100%): IR ($CHCl_3$) 3100−2300, 1668, 1597 cm^{-1}; HRMS (FAB) calcd for $C_{11}H_{22}N_4$−H 209.1766, found 209.1757.

(1*RS*,8b*SR*)-2-Hexahydro-1*H*,3*H*,6*H*,8b*H*-2a,5a,8a-triazaacenaphthylen-1-yl)ethylammonium Chloride (25). A solution of (1*RS*,8b*SR*)-2-(hexahydro-1*H*,3*H*,6*H*,8b*H*-2a,5a,8a-triazaacenaphthylen-1-yl)ethylamine (**23**; 378 mg, 1.80 mmol) in dry CH_2Cl_2 (10 mL) was stirred at 25 °C under dry N_2 and treated with dry gaseous HCl (42.4 mL, 63.6 mg, 1.74 mmol), added slowly by syringe. Volatiles were then removed by evaporation under reduced pressure, and the residue was triturated with ether and dried *in vacuo* to give (1*RS*,8b*SR*)-2-hexahydro-1*H*,3*H*,6*H*,8b*H*-2a,5a,8a-triazaacenaphthylen-1-yl)ethylammonium chloride (**25**; 432 mg, 1.74 mmol, 100%) as a colorless solid. Recrystallization from CH_2Cl_2 or $CHCl_3$ provided an analytically pure sample: mp 152−154 °C dec; IR ($CHCl_3$) 3100, 2471 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$) δ 1.55 (dquint, ^2J = 13.0 Hz, ^3J = 2.7 Hz, 1H, H_{4e}), 1.59 (dquint, ^2J = 13.5 Hz, ^3J = 2.7 Hz, 1H, H_{7e}), 1.69−1.74 (m, 1H, H_9), 1.81−1.87 (m, 2H, H_{5a} and H_{6a}), 1.89−1.99 (m, 2H, H_{4a} and H_{7a}), 2.04 (ddd, ^2J = 11.9 Hz, ^3J = 10.5, 2.7 Hz, 1H, H_{3a}), 2.16 (s, 1H, H_{8b}), 2.21 (ddd, ^2J = 11.9, 10.7, 2.7 Hz, 1H, H_{8a}), 2.24−2.29 (m, 1H, $H_{9'}$), 2.48 (dd, ^2J = 9.4 Hz, ^3J = 9.4 Hz, 1H, H_{2a}), 2.84−2.87 (m, 2H, H_{5e} and H_{6e}), 2.94−2.97 (m, 1H, H_{1a}), 2.99 (dd, ^2J = 9.4 Hz, ^3J = 2.6 Hz, 1H, H_{2e}), 3.02−3.07 (m, 1H, H_{3e}), 3.18−3.24 (m, 3H, H_{8e}, H_{10}, and $H_{10'}$); ^{13}C NMR (150 MHz, $CDCl_3$) δ 24.5 (C_4), 25.1 (C_7), 27.3 (C_9), 36.6 (C_{10}), 47.3 (C_8), 49.6 (C_3), 51.5 (C_5), 51.8 (C_6), 53.1 (C_2), 56.2 (C_1), 98.7 (C_{8b}). Anal. Calcd for $C_{11}H_{23}ClN_4$: C, 53.54; H, 9.39. Found: C, 53.07; H, 9.12.

Pyrolysis of (1*RS*,8b*SR*)-2-Hexahydro-1*H*,3*H*,6*H*,8b*H*-2a,5a,8a-triazaacenaphthylen-1-yl)ethylammonium Chloride (25). In a glovebox under dry Ar, one arm of an H-tube was charged with (1*RS*,8b*SR*)-2-hexahydro-1*H*,3*H*,6*H*,8b*H*-2a,5a,8a-triazaacenaphthylen-1-yl)ethylammonium chloride (**25**; 114 mg, 0.462 mmol) and the other with a mixture of *trans*-stilbene (82.7 mg, 0.459 mmol) and 10% Pd on carbon (90 mg) in deoxygenated absolute C_2H_5OH (15 mL). The tube was sealed, and the arm containing the salt was heated in an oil bath at 145 °C for 44 h. The tube was then cooled and opened under Ar. The pyrolysate was taken up in CH_3OH (10 mL), and the mixture was treated with a saturated solution of HCl in CH_3OH. Volatiles were removed by evaporation

under reduced pressure, and the residue was again taken up in CH_3OH and treated with HCl. Evaporation yielded pure 2-(hexahydro-1*H*,3*H*,6*H*-5a,8a-diaza-2a-azoniaacenaphthylen-1-yl)ethylammonium dichloride (**24**: 107 mg, 0.380 mmol, 82%), which had ^{1}H and ^{13}C NMR spectra identical with those of an authentic sample.

The ethanolic suspension was removed from the other arm of the the H-tube and filtered, and solvent was removed by evaporation under reduced pressure. The residue was redissolved in $CHCl_3$ (5 mL), and the solution was cooled to 0 °C, stirred, and treated dropwise with a solution of Br_2 (74.9 mg, 0.469 mmol) in $CHCl_3$ (2 mL). The mixture was kept at 25 °C for 1 h, and then volatiles were removed by evaporation under reduced pressure. Preparative thin-layer chromatography (silica, hexane) of the residue provided 1,2-diphenylethane (32.7 mg, 0.181 mmol), which corresponds to a 39% yield of H_2 evolved during the pyrolysis.

Relative Reactivity of Orthoformamides 1, 25, and 29. Orthoformamide **25** (0.20 mmol) and equimolar mixtures of orthoformamides **1** and **29**[15] (0.20 mmol) with butylammonium chloride (0.20 mmol) were dissolved separately in DMSO-d_6 (0.5 mL). The three solutions were degassed, sealed *in vacuo* in NMR tubes, and heated at 120 °C. The extent of reaction and the identity of the product were determined by ^{1}H and ^{13}C NMR spectroscopy.

X-ray Crystallographic Study of (1*RS*,8b*SR*)-(Hexahydro-1*H*,3*H*,6*H*,8b*H*-2a,5a,8a-triazacenaphthylen-1-yl)-acetonitrile (22).[23] Crystals of orthoformamide **22** belong to the monoclinic space group $P2_1/c$ with a = 7.397(2) Å, b = 15.983(5) Å, c = 9.706(3) Å, β = 97.35(2)°, V = 1138.1(6) Å^3, D_{calcd} = 1.204 g cm^{-3}, and Z = 4. Data were collected at 295 K, and the structure was refined to R_f = 0.086, R_w = 0.082 for 1519 reflections with $I > 1.96\sigma(I)$.

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Supporting Information Available: ^{1}H and ^{13}C NMR spectra of compounds **8**, **17**, and **21** (6 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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(23) The authors have deposited X-ray crystallographic data, a description of the structure determination, and tables of atomic coordinates and isotropic thermal parameters, bond lengths and angles, anisotropic thermal parameters, and refined and calculated hydrogen atom coordinates with the Cambridge Crystallographic Data Centre. The data can be obtained, on request, from the Director, Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK.