3970 J. Am. Chem. Soc. 1988, 110, 3970-3979

Electron-Rich Hexasubstituted Benzene Derivatives and Their Oxidized Cation Radicals, Dications with Potential Triplet Ground States, and Polycations[1]

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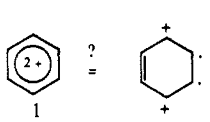
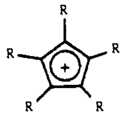
Abstract: Five new benzene derivatives have been synthesized carrying electron-releasing substituents. The derivative of hexaaminobenzene with six ethano bridges connecting all the nitrogens can be reversibly oxidized all the way to a tetracation; the dication is a (ground-state) triplet species. Two derivatives of 1,3,5-trihydroxy-2,4,6-triaminobenzene were also prepared, as well as two derivatives of 1,3,5-triaminobenzene-2,4,6-trithiol. In these cases three ethano bridges connected heteroatoms. Cation radicals could be prepared in all cases, and with one of the oxygen compounds a triplet-state dication was also prepared. The synthetic procedures involved an unusual "zipper" cyclization in the hexaaza series.

The benzene ring normally contains a stable 6π-electron aromatic system. The benzene dication system **1**, with four π electrons, is very different. It may well be antiaromatic, i.e., destabilized by conjugation.[2] More generally, benzene dication derivatives with appropriate symmetry may have ground triplet states, with two unpaired electrons.



1

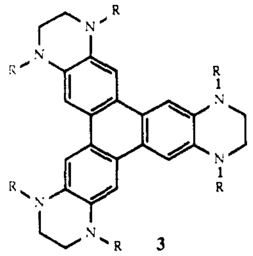
In the cyclopentadienyl cation series **2** the triplet question has been explored fairly carefully.[3] The parent cation is indeed a ground-state triplet,[4] the pentachlorocyclopentadienyl cation is also a ground-state triplet,[5] but pentaphenylcyclopentadienyl cation has a singlet ground state with a very low lying triplet excited state.[6] The first two examples have the fivefold symmetry that leads to orbital degeneracy and unpairing of the highest two electrons, but in the pentaphenyl case there is apparently geometric distortion that lowers the singlet state below the symmetrical triplet. Some cyclopentadienyl cations with substituted phenyls have been explored;[7] these are also ground-state singlet species with low-lying triplet states.



2

The requirement for orbital degeneracy that can lead to a stable triplet state is C_3 symmetry or greater. Thus, symmetrically substituted derivatives of triphenylene dication can also have ground triplet states. Parker originally reported the preparation of the hexamethoxytriphenylene dication and the observation of a triplet ESR spectrum.[8] We have confirmed that this ESR spectrum follows the Curie law, at least over a reasonable temperature range, and therefore probably reflects a triplet ground state.[9] (It is important that such studies be routinely done. Pentaphenylcyclopentadienyl cation had exhibited a triplet ESR spectrum, and only a Curie law study revealed the fact that the triplet was a thermally accessible excited state, not the ground state.[6])

We have described a series of triphenylenes with six amino substituents, the hexaazatritetralins (**3**) and their derived stable cations and dications.[10,11] The dications of three examples of this species are ground-state triplets, as judged by Curie law studies. They have been examined as potential components of an organic ferromagnet,[11] on the basis of theoretical concepts that will be mentioned later in this paper.



3

The triplet-state cyclopentadienyl cations prepared so far are not stable molecular species under normal conditions. They can be prepared only at very low temperatures and undergo decomposition reactions on warming even below room temperature. By contrast, the hexaazatritetralin system **3** forms stable monocations and dications that can be handled under normal reaction conditions if they are protected from moisture.[10,11] However, the hexaazatritetralin system has a rather large conjugated center. It is predicted[12] that the energetic advantage of a triplet state over a singlet state will diminish as a conjugated system gets larger (the large size of the conjugated system is probably one of the reasons that the singlet state fell below the triplet state in pentaphenylcyclopentadienyl cation). For this reason it has seemed to us of considerable interest to learn how to prepare stable derivatives of benzene dication, with a relatively small benzene core and simple electron donor substituents.

Our interest in doing this was stimulated by the finding by Wasserman, some years ago, that the dication **4** derived from

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(1) Taken from: Thomaides, J. S. Ph.D. Thesis, Columbia University, 1987.

(2) Breslow, R. *Acct. Chem. Res.* **1973**, *6*, 393.

(3) Breslow, R. In *Topics in Nonbenzenoid Aromatic Chemistry*; Nozoe, T., Breslow, R., Hafner, K., Ito, S., Murata, I., Eds.; Hirokawa: Tokyo, 1973; Vol. I.

(4) Saunders, M.; Berger, R.; Jaffe, A.; McBride, J. M.; O'Neill, J.; Breslow, R.; Hoffman, J. M., Jr.; Perchonock, C.; Wasserman, E.; Hutton, R. S.; Kuck, V. J. *J. Am. Chem. Soc.* **1973**, *95*, 3017.

(5) Breslow, R.; Hill, R.; Wasserman, E. *J. Am. Chem. Soc.* **1964**, *86*, 5349.

(6) Breslow, R.; Chang, H. W.; Yager, W. A. *J. Am. Chem. Soc.* **1963**, *85*, 2033.

(7) Broser, W.; Kurreck, H.; Siegle, P. *Chem. Ber.* **1967**, *100*, 788. Broser, W.; Siegle, P.; Kurreck, H. *Ibid.* **1968**, *101*, 69.

(8) Bechgaard, K.; Parker, V. D. *J. Am. Chem. Soc.* **1972**, *94*, 4749.

(9) Kluttz, R. Q. Ph.D. Thesis, Columbia University, 1980.

(10) Breslow, R.; Jaun, B.; Kluttz, R. Q.; Zia, C.-Z. *Tetrahedron* **1982**, *38*, 863.

(11) LePage, T.; Breslow, R. *J. Am. Chem. Soc.* **1987**, *109*, 6412.

(12) Cf.: McGlynn, S. P.; Azumi, T.; Kinoshita, M. *Molecular Spectroscopy of the Triplet State*; Prentice-Hall: Englewood Cliffs, NJ, 1979.

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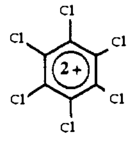
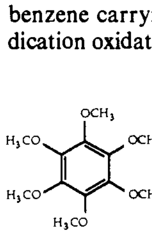
hexachlorobenzene is a ground-state triplet, as judged by the usual Curie law criterion.[13] Although with six chlorine atoms this dication is not a chemically stable species and seems an unlikely component of systems to test theories about possible ferromagnetic organic solids, the finding that it was apparently a ground-state triplet species was reassuring. Not all molecules that could have ground triplet states are found to be triplets. For instance, cyclobutadiene apparently exists in a rectangular geometry, which results in a splitting of the two orbitals that would be degenerate in a square geometry, and it exists as a singlet species.[14] One of the purposes of our exploration in this area is to establish which cases are indeed true ground-state triplet species and which undergo a distortion of some sort to pair up the electrons.



4

A number of years ago we set out to prepare derivatives of benzene carrying strong electron donor groups, to stabilize the dication oxidation state. We found that hexamethoxybenzene (**5**) undergoes an irreversible one-electron oxidation, so six oxygen atoms in this structure are not enough.[15] Two 1,3,5-triaminobenzene derivatives **6** and **7** also underwent irreversible oxidation, possibly because the unsubstituted positions are available for further reaction in the cations.[15] We prepared hexakis(dimethylamino)benzene (**8**) and found that it was not reversibly oxidized either.[15] Its irreversible oxidation potentials were actually higher than those of **6** or **7**, presumably because the six dimethylamino groups are so badly twisted by steric interaction that they are not as effective as three coplanar dimethylamino groups at stabilizing the cation. To solve this problem, we selected the hexaaminobenzene derivative octadecahydrohexaazacoronene (HOC, **9**) as our synthetic target.[9,16]



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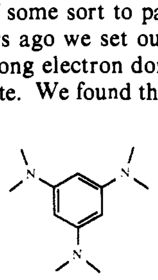

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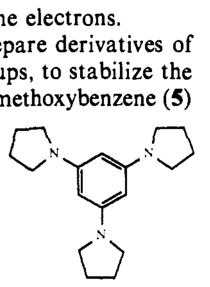

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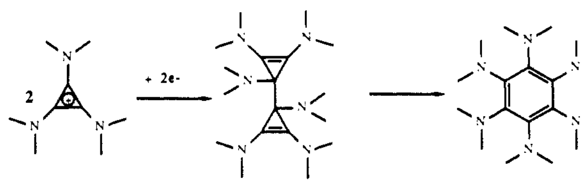

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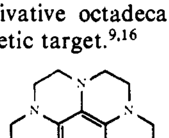
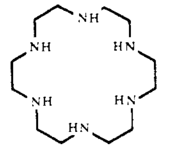


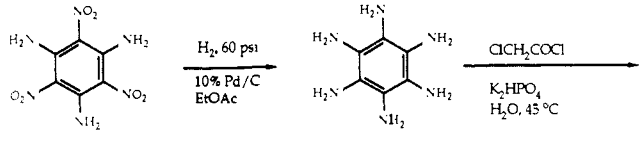
9, HOC

Several approaches to this target compound HOC were examined in our laboratory. We had found that hexakis(dimethylamino)benzene (**8**) could be conveniently prepared by reductive dimerization of the tris(dimethylamino)cyclopropenium cation; the dimer spontaneously rearranged under the reduction conditions.[15,17] An analogous scheme involving triaziridinocyclopropenium cation failed at an early stage.[9] We also considered schemes for inserting a benzene ring into the center of hexacyclen (**10**). Various approaches to this process were unsuccessful,[9,18] and we eventually decided to construct the system in a somewhat more classical manner.[19,20]

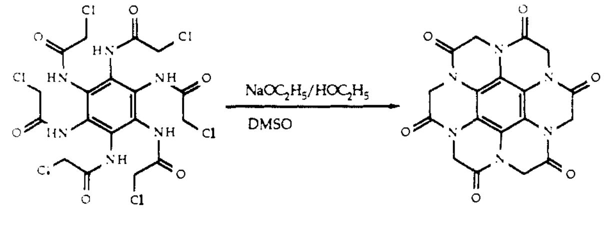


10

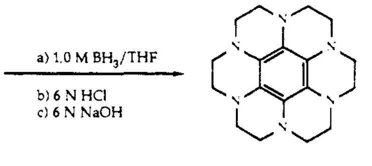
1,3,5-Trinitro-2,4,6-triaminobenzene (**11**) is readily prepared by a literature procedure.[21] It had been reported[22] that this could be reduced to hexaaminobenzene (**12**) with phenylhydrazine, but in our hands this is a poor reaction. Catalytic hydrogenation was quite effective, as we reported in our preliminary communication,[19] and produced a solution of the hexaamine. Because this is an air-sensitive compound, we generally acylated it directly.



11　　**12**



13　　**14**



9, HOC

More recently, Rogers has reported[23] that the trinitro compound **11** can be reduced with sodium and ammonia to produce hexaaminobenzene (**12**). This may also be a useful procedure, although we have had reports that it is difficult for others to repeat.

The crude hexaaminobenzene (**12**) was readily converted to the known hexaacetamide,[22] and with chloroacetyl chloride we could prepare the hexakis(chloroacetamido)benzene (**13**) in 40–60% overall yield from the trinitro compound **11**. Interestingly, the mass spectrum of this species showed the expected parent ion but also an intense peak at mass 409 corresponding to (M + 1) of the fully cyclized hexalactam **14**. This suggested that the

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(13) Wasserman, E.; Hutton, R. S.; Kuck, V. J.; Chandross, E. A. *J. Am. Chem. Soc.* **1974**, *96*, 1965.

(14) Masamune, S.; Souto-Bachiller, F. A.; Machiguchi, T.; Bertie, J. A. *J. Am. Chem. Soc.* **1978**, *101*, 4889.

(15) Johnson, R. W. Ph.D. Thesis, Columbia University, 1976.

(16) Breslow, R. *Pure Appl. Chem.* **1982**, *54*, 927. Breslow, R. *Mol. Cryst. Liq. Cryst.* **1985**, *125*, 261.

(17) Johnson, R. W. *Tetrahedron Lett.* **1976**, 589.

(18) Etter, M. C.; Richman, J. E. *J. Org. Chem.* **1985**, *50*, 112.

(19) Breslow, R.; Maslak, P.; Thomaides, J. S. *J. Am. Chem. Soc.* **1984**, *106*, 6453.

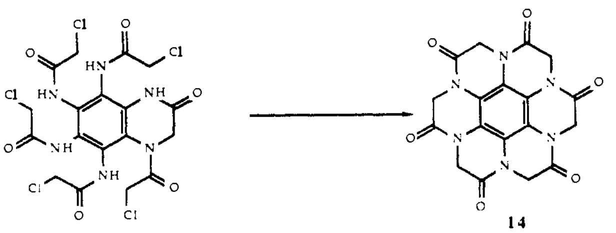
(20) A report of a synthesis of HOC nearly identical with ours appeared after the publication of our synthesis of HOC: Kohne, V. B.; Praefcke, K.; Reichmann, A. *Chem.-Ztg* **1985**, 17.

(21) (a) Backer, H. J.; Van der Baan, Sj. *Recl. Trav. Chim. Pays-Bas* **1937**, *56*, 1175. (b) Jackson, C. L.; Wing, J. F. *Am. Chem. J.* **1887**, *9*, 348. (c) Jackson, C. L.; Wing, J. F. *Am. Chem. J.* **1888**, *10*, 282.

(22) Flürscheim, B.; Holmes, E. L. *J. Chem. Soc.* **1929**, *330*.

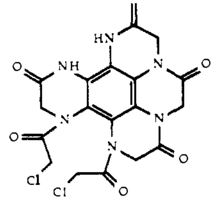
(23) Rogers, D. Z. *J. Org. Chem.* **1986**, *51*, 3904.

cyclization we wished to perform occurred readily in the mass spectrometer. Treatment of the hexakis(chloroacetyl) derivative **13** with 6.4 equiv of sodium ethoxide produced the desired hexalactam **14** in 75–85% yield.



14

The clean formation of **14** is quite interesting. It requires six intramolecular alkylations, and they must all be in the same relative direction. That is, if the first cyclization goes in a clockwise direction then all the other cyclizations must also be clockwise for the correct product to form. If at any point another cyclization had occurred in the wrong direction, perhaps on the other side of the molecule, then side products such as **15** or **16** should have



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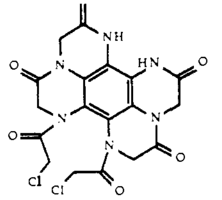


16

been seen. However, we saw no evidence for any such materials. If the cyclization direction had been completely random, the calculated product distribution is 46% **14**, 37% **15**, and 17% **16**. More than half the material should have been the wrong products, but none were found.

When we conceived this synthesis, we hoped that the initial alkylation would facilitate alkylation of the neighboring group, leading to a zipperlike closing to form only product **14**. The fact that we formed more than the expected statistical amount of **14**, and could not detect any of **15** or **16**, suggested that this idea is correct.

An independent piece of evidence in support of this concept was obtained by treating the hexakis(chloro amide) **13** with only 2 equiv of sodium ethoxide. This led to the formation of the hexalactam **14** in 99% of the theoretical (33%) yield and recovered starting material in 94% of the theoretical (67%) yield. Thus, once the first cyclization occurs the rest of them occur more readily, so we find only completely cyclized material or completely uncyclized material. This is expected if there is indeed some driving force for cyclization once the first closure has occurred.

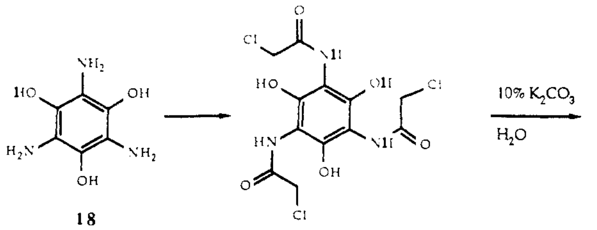
Since the original hexakis(chloro amide) **13** is very crowded, and must exist with the groups twisted out of the plane, there are two obvious ways in which the first cyclization might facilitate neighboring closures. In one model, cyclization onto a nitrogen atom brings its own chloroacetyl group into the plane, in a position to attack the next nitrogen along. In a second model, cyclization of one group makes its NH group rotate into the benzene plane, and this may acidify it or in some other way make it more easily alkylated. Thus, one of these models leads to an increased activity of the chloroacetyl group of a partially cyclized system, while the other postulates an increased activity of the NH group in such a partially cyclized system. Whatever the cause, the result is a remarkably effective cyclization to the desired hexakis(lactam) **14**.

We had selected **14** as an intermediate target since we expected the fully reduced hexaamine **9** to be quite air reactive and difficult to handle. As we hoped, the corresponding hexakis(lactam) **14** is sufficiently deactivated that it can be readily handled, although it is quite an insoluble compound. The best reducing agent for the conversion of a hexaamide to a hexaamine in the triphenylene series **3** had been BH_3, and this reagent was effective here as well. The desired product HOC (**9**) could be isolated from the reduction of **14** in 60–80% yield. HOC was quickly oxidized by air, even as a solid, so it was handled under argon with syringe or Schlenk techniques, or in a controlled atmosphere glovebox. Even in the absence of air HOC darkened in solutions of CH_2Cl_2 or $CHCl_3$. It was readily converted to the cation radical or to the dication, whose properties will be described subsequently.

Compounds with three nitrogens and three oxygens, or three nitrogens and three sulfur atoms, are also of interest. They would clearly not be as easily oxidized, but we thought that these substituents might be enough to make the dication state chemically accessible. In systems with C_3 symmetry such dications also have the potential to have triplet ground states.

For the synthesis of compounds with three nitrogens alternating with three oxygens on a benzene ring we selected the tris(lactam) **17** as an intermediate target. Again, we hoped that with amide rather than amine groups we would have an intermediate that could easily be isolated and purified and later converted by reduction to the more sensitive final product. In our first synthesis we prepared 1,3,5-trifluoro-2,4,6-trinitrobenzene[24] and displaced the three fluorines with ethyl glycolate. Reduction of the three nitro groups with hydrogen, and cyclization of the resulting triamine, afforded the tris(lactam) **17** in only 9% yield.

A better synthesis started with triaminophloroglucinol (**18**), an air-sensitive compound that we prepared by an improved version of the literature scheme.[25] The compound was triacylated on nitrogen with chloroacetyl chloride, under acidic conditions, and the resulting triamide **19** was then cyclized with K_2CO_3. Remarkably, a mixture of two different cyclization products was formed, with the desired **17** being produced in only 35% yield while the undesired material **20** was produced in 47% yield. In contrast to the zipper mechanism that produced entirely the correct isomer in the cyclization of our hexaamide **13**, the cyclization of **19** has a preference for forming the wrong compound **20**. On a purely statistical[26] basis, **20** should have been the minor 33% product.



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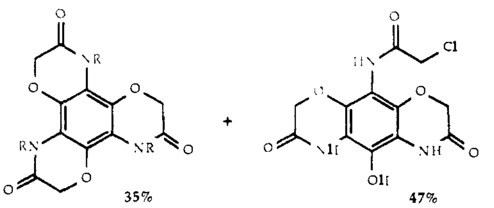
19



17, R = H

20

21. R = Me

The tris(lactam) **17** was methylated in the standard way to form tris(lactam) **21**, and these two tris(lactams) were reduced with BH_3 to the corresponding tris(dehydromorpholine) derivatives **22** and **23**. The methylated compound **23** (BONM)[27] was stable in air, while the unmethylated analogue **22** (BONH)[27] underwent

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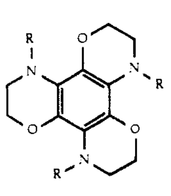
[24] Shaw, G. C., III; Seaton, D. L. *J. Org. Chem.* **1961**, *26*, 5227.

[25] Quadbeck, G.; Röhm, E. *Chem. Ber.* **1956**, *89*, 1645.

[26] After the first cyclization, there are three ways the second can occur. We assume that they have equal probability, for the statistical calculation; two of them lead ultimately to the fully cyclized product.

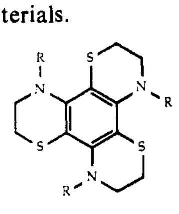
[27] The acronyms chosen are symbolic, except for HOC. Thus, the symbol BONM refers to our benzene ring carrying three O's and three N's, with a methyl group on the N's. BSNH has three S's and three N's, with H on the N's.



22: R = H, BONH
23: R = Me, BONM

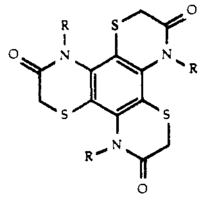
air oxidation in solution. As will be described, both compounds could be easily oxidized to cations of interest.

We prepared the related compounds **24** and **25** in which three sulfur atoms replaced the three oxygens of **22** and **23**. We expected that these sulfur atoms would change the oxidation potentials and that they should be of interest with respect to the solid-state properties of the compounds. Sulfur atoms on the edge of an electrically conducting organic stack can facilitate sideways interactions between stacks, turning one-dimensional conduction into a multidimensional process.[28] With respect to the problem of preparing ferromagnetic solids, it was very desirable to have the prospect of sulfur multidimensional communication between stacks of organic materials.



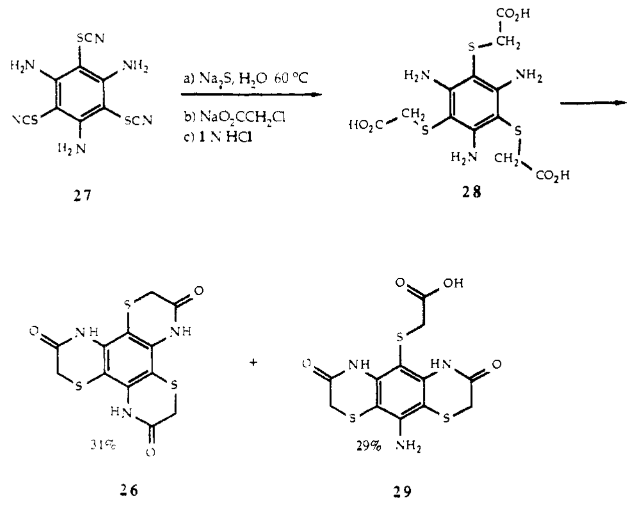
24: R = H, BSNH
25: R = Me, BSNM

Grandolini and Martani had already reported the synthesis of the tris(lactam) **26**, which was our intermediate target compound.[29]



26: R = H
31: R = Me

We were able to produce **26** by a modification of their procedure. 1,3,5-Triaminobenzene reacts with ammonium thiocyanate and a chlorinating agent to produce the trithiocyanato derivative **27**.



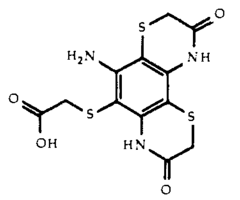
The cyano groups were removed with sodium sulfide, and the intermediate trithiol was immediately alkylated with sodium chloroacetate. The resulting triamino triacid cyclized on acidification to produce both the desired tris(lactam) **26** and the undesired product **29**. In this case the desired product could be isolated in 31% yield, while the undesired material was present in an essentially equivalent 29% yield. Since statistics[26] would lead to a 2:1 preference for the desired compound, here too we are getting a less than statistical production of the compound of interest. The finding of a mixture here and in the cyclization of the oxygen compound once again makes it clear how remarkable was the highly selective cyclization in the hexaaza series.

Table I. Donor Oxidation Potentials Determined by Cyclic Voltammetry in CH_3CN vs Ag/0.01 M $AgNO_3$[j]

	E_1,[a] mV	E_2, mV	E_3, mV	E_4, mV	ΔE,[b] mV	T, °C
HOC (**9**)	−771	−285	178	556	486	25
BONH (**22**)	−163	449[c]			612	25
	−159	395[d]			554	−44
BSNH (**24**)	−24	528	960[c]		552	25
	−32	478	915[d]	1400[c]	510	−44
BONM (**23**)	2	392[d]			390	25
	36	356			320	−44
BSNM (**25**)	293	524	873	1113[c]	231	25
Et_6-HAT[e,h]	−262	−14	194	521	248	ambient
$(CF_2HCH_2)_6$-HAT[f,h]	26	243	460	820	217	ambient
$(CF_3CH_2)_6$-HAT[g,h]	149	393	621	987	244	ambient
TMPD[i]	−195	387			582	25

[a] $\sigma = \pm 10$ mV for all oxidation potentials. [b] $E_2 - E_1$. [c] Wave was completely irreversible. [d] Wave was only quasi-reversible. [e] **3**, R = Et. [f] **3**, R = CF_2HCH_2. [g] **3**, R = CF_3CH_2. [h] Reference 11. [i] Tetramethyl-*p*-phenylenediamine. [j] Add 310 mV to refer these potentials to SCE.

Grandolini and Martini had reported a side reaction as well, but they had assigned the structure **30** to the side product.[29]



30

However, our assignment of **29** for this structure seems secure. The NMR spectrum shows only one set of lactam methylene proton resonances, in a 2:1 ratio relative to the uncyclized acid methylene proton resonances. Only one amide NH resonance was found in this side product. Barring accidental coincidences, these results are consistent with our assigned structure **29** but not the alternative **30**. Furthermore, alternative **30** must be postulated to be simply the result of an incomplete cyclization of the starting system, but we found that the ratio of **26** to **29** did not change if we carried out the cyclization for a further period of time.

Grandolini and Martani had supported their structure assignment with the finding that the side product (**29**, **30**) was converted to the desired product **26** on treatment with acidic ethanol. We confirmed this transformation, but of course it is a perfectly reasonable process from our assigned structure **29** as well, by a series of reversible cyclizations and cleavages. Since the side product **29** was converted to the desired product **26** in 88% yield by this subsidiary treatment, the overall synthesis is very convenient. This tris(lactam) **26** could be methylated on nitrogen under standard conditions, and the resulting tris(lactam) **31** was reduced to the tris(dehydrothiomorpholine) derivative **25** (BSNM)[27] with BH_3. In the same way the unmethylated compound **24** (BSNH)[27] was produced from the tris(lactam) **26**. Thus, as a result of these syntheses five novel benzene derivatives were available, each carrying six electron donor substituents geometrically constrained to facilitate conjugative interaction.

Oxidation to the Cations. Cyclic voltammetry was used to determine the oxidation potentials of our five electron-rich benzene derivatives: HOC (**9**), BONH (**22**), BONM (**23**), BSNH (**24**), BSNM (**25**). The results are listed in Table I, along with the data for three triphenylene derivatives we have reported elsewhere and

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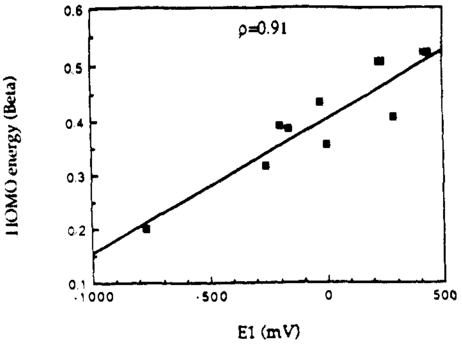


Figure 1. Plot of the HOMO energy (from an HMO calculation) vs the measured E_1 for molecules in Table I.

for *N,N,N′,N′*-tetramethyl-*p*-phenylenediamine.

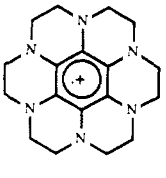
HOC (**9**) shows *four* reversible oxidation waves, corresponding to the successive formation of a cation radical, dication, trication, and tetracation. The last species is the first example of a benzene derivative with two π electrons instead of six, although of course this is only a formality, since the nitrogen electrons are strongly involved. When three of the six nitrogens are replaced by oxygens, in BONM (**23**), the compound is much more resistant to oxidation. Only two oxidation waves are seen, and the second one is fully reversible only at −44 °C. In the corresponding compound without the methyls, BONH (**22**), again only two waves are seen, and the second one is not fully reversible even at −44 °C.

With three sulfurs instead of three oxygens the potentials are even more positive, but now with the methyl groups present BSNM (**25**) shows three reversible waves, and an irreversible fourth, at 25 °C. Without the *N*-methyl groups BSNH (**24**) has only two reversible waves at 25 °C, with somewhat better behavior at −44 °C. The poor electrochemistry in some of these cases must reflect chemical reaction. Such complications are seen particularly in the NH compounds, whose cations can lose protons.

The potentials for the first oxidation wave can be correlated with simple HMO theory, as has been described for other systems.[30,31] We used standard coulomb and resonance integral parameters[30,31] and plot the resulting correlation in Figure 1. The biggest deviations are seen with the two methylated compounds BONM and BSNM. Models suggest that these methyl groups may crowd the oxygen or sulfur. This could force some nonplanarity of the amino groups so as to diminish their stabilizing ability, as observed.

The gap between E_1 and E_2 is of some interest in these series and is also listed in Table I. As expected, the gap is smaller in the triphenylene series, with a large delocalized system to diminish charge–charge interactions, than in the benzene series.

HOC was easily oxidized to the stable cation radical **32**, and a variety of crystalline salts of this cation could be prepared. All showed the same UV–vis spectrum, but only the $HOC^+SbF_6^-$ salt was prepared in analytical purity. Unfortunately, to date all these salts are microcrystalline, not suitable for X-ray crystallography.



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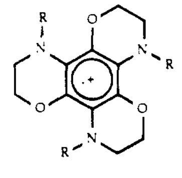
The ESR spectrum of HOC^+ (**32**) in ethanol shows 25 evenly spaced lines, corresponding to hyperfine coupling by 6 equivalent nitrogens and only 12 protons; the hyperfine coupling constant for N and for H are equal, within experimental error, at 2.63 G. This spectrum indicates that the ethano units in HOC^+ (**32**) are not in the benzene plane but show strong coupling by 12 pseudo-axial protons and weak coupling by the other 12 pseudo-equatorial protons. Ring flips are slow on the ESR time scale, in part because *all six* ethano units would have to flip to interconvert axial and equatorial protons. The nitrogen hyperfine coupling constant of 2.63 G is close to that we calculate (2.53 G) from the nitrogen spin density, by an HMO calculation, and the usual McConnell-type equation[32,33] relating spin density to coupling constant.

Figure 2. ESR spectrum of HOC dication **35** in CH_2Cl_2/CH_3CN (1.2:1).

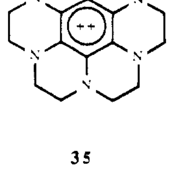
The benzene derivatives with three of the nitrogens replaced by oxygens or sulfur atoms did not form such well-behaved cation radicals, consistent with our electrochemical findings. Solutions of BONM (**23**) were oxidized with I_2 or with tris(*p*-bromophenyl)aminium hexafluoroantimonate[34] to the cation radical $BONM^+$ (**34**), which gave a complex multiline ESR spectrum. The sample decomposed over 24 h. A solid salt of $BONM^+$ was prepared with 1 equiv of $NO^+PF_6^-$ in CH_3CN, but it could not be purified.



33 R = H
34 R = Me

Interestingly, the corresponding cation without methyl groups (**33**) was somewhat more stable. Oxidation of BONH (**22**) with 1 equiv of Br_2 afforded $BONH^+ Br^-$ as a dark blue solid that in trifluoroethanol solution gave a broad poorly resolved signal in the ESR. This solution was stable when protected from air. In the sulfur series, both BSNM (**25**) with methyl groups and BSNH (**24**) without them gave poorly stable cations on oxidation, the ESR signals and green colors fading over the course of an hour or so.

The ease of formation of the dications and the question of whether they have triplet ground states are the principal matters of interest. In the HOC series a stable HOC^{2+} (**35**) could be easily



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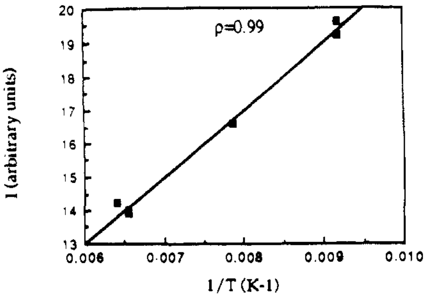


Figure 3. Curie plot of the intensity of the $\Delta m = 2$ line in the triplet ESR spectrum of Figure 2 vs $1/T$. The line through the points is the computer-generated best fit. The fit to a Curie plot is consistent with the triplet being the ground state of the species.

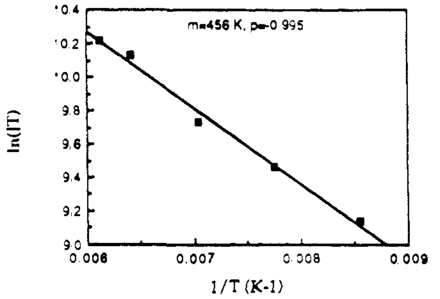


Figure 4. Plot of intensity and temperature for the $\Delta m = 2$ line of the triplet spectrum of HOC dication in 100% CH_3CN. The form of the relationship indicates a low-lying triplet that is not the ground state, in contrast to the situation of Figure 3. The change in solvent has produced this change in the ordering of the states.

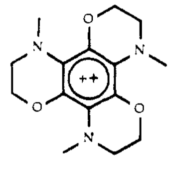
prepared. Solutions were made by oxidation of HOC^+ with I_2, Br_2, or $NO^+SbF_6^-$ or by oxidizing solid samples of HOC with excess NO^+SbF_6. An analytically pure sample of $HOC^{2+}(I_3^-)_2$ was prepared by treatment of an ethanol solution of HOC^+I^- with excess I_2. The species **35** has λ_{max} 523 nm (ϵ 15 000) in CH_3CN solution, giving it a red-purple color.

In the ESR HOC^{2+} (**35**) in CH_3CN/CH_2Cl_2 showed a triplet spectrum (Figure 2) with signals at 1580 ($\Delta m = 2$), 2640, and 3900 G (*z* lines) and 2936 and 3558 G (*xy* lines). From these line positions, the spectroscopic parameter *E* is <0.0002 cm^{-1} and $D = 0.067 \pm 0.002$ cm^{-1}. The *D* value is smaller than the value 0.1012 cm^{-1} for the unstable dication derived from hexachlorobenzene,[13] as expected, since in the hexaamino derivative HOC^{2+} more of the spin density will be delocalized onto the heteroatoms. However, the *D* value for **35** is larger than that for our hexaaminotriphenylene dications (e.g., 0.022 cm^{-1} for the dication of **3** with R = Et), in which the spins are delocalized over a larger central core.[10,11]

The question of whether this observed triplet state of HOC^{2+} is indeed the ground state is complex. We found (Figure 3) that in CH_2Cl_2/CH_3CN it reversibly obeyed the Curie law $I = C/T$ as expected for a ground-state triplet over the temperature range 109–156 K, but we did not examine a larger range. Most seriously, when the same dication was prepared in pure CH_3CN it did not follow the Curie law, as a ground-state triplet should, but instead followed a law (Figure 4) that indicated that the triplet state is 0.9 kcal/mol above the ground singlet state. The line positions in this solvent were slightly different at 1562, 2640, 3820, 2900, and 3500 cm^{-1}.

Similar changes from ground state to low-lying excited-state triplets have been seen for other species as a function of solvent.[35,36] They probably reflect the shift from species in a symmetrical environment to species in an environment distorted by localized ion pairing. In any case, it seems clear from these results that even if the isolated dication HOC^{2+} (**35**) is a ground-state triplet, the singlet state cannot be very far away. Consistent with this, a DMSO solution of the crystalline bis(triiodide) salt of HOC^{2+} did not show a triplet ESR spectrum at all.

We were also able to prepare the dication (**36**) of BONM in solution. Reaction of BONM with 2 equiv of NO^+ SbF_6^- in CH_3CN at −78 °C produced a blue-green solution that turned deep purple when the NO was pumped away. When frozen, this solution exhibited a typical triplet ESR spectrum, with lines at 1577 ($\Delta_m = 2$), 2678, and 3860 G (*z* lines) and 2938 and 3528 G (*xy* lines). From this $E < 0.0002$ cm^{-1} and $D = 0.064 \pm 0.002$ cm^{-1}, almost the same values as for HOC^{2+}. This dication was unstable at room temperature but followed the Curie law over the range 104–165 K. Thus, it is apparently also a ground-state triplet, as judged by this limited study.



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We were not able to produce triplet ESR spectra from the oxidation of the other three compounds, BONH, BSNH, and BSNM. Since we could not produce stable samples of characterized dications either, we do not yet know if these dications were indeed produced in solution but do not show triplet signals.

The Ferromagnet Question. We have described elsewhere[16] our approach to the McConnell proposal for ferromagnetic interaction in organic solids. In this scheme cation radicals whose corresponding dication is a ground-state triplet are paired in a charge-transfer solid with appropriate anion radical acceptor species. Other schemes have also been advanced by which our triplet-state species might be used in the construction of organic ferromagnets.[37]

We have recently described a study of this question using the triphenylene derivatives that we had synthesized earlier.[11] Further work will be needed to see whether the new species described here can be used in any of these approaches to ferromagnetism. However, they have that potential. In any case, with the strong electron-donating conjugation in our systems we have prepared for the first time some neutral benzene derivatives that are so easily oxidized that the dication state is readily available. For HOC the dication is a stable high-spin species with rather normal chemical properties.

Experimental Section

General Procedures. Reactions in which the products or reagents were moisture or air sensitive were done under anhydrous/anaerobic conditions on the bench top or under argon in a Vacuum Atmospheres Co. Model HE 43-2 drybox equipped with a Vacuum Atmospheres HE-493 Dri-Train oxygen and moisture remover.

All chemical reagents used were from Aldrich Chemical Co. or Alfa Products unless otherwise specified. Solvents used were from Fisher Scientific, Amend Drug and Chemical Co., or EM Science. For anhydrous work, CH_2Cl_2, benzene, and CH_3CN were distilled from CaH_2 under argon, and THF and diethyl ether were distilled from potassium/benzophenone under argon. For use in the glovebox, CH_2Cl_2 was shaken with H_2SO_4 prior to distillation from CaH_2, and CH_3CN was distilled from $KMnO_4$ prior to distillation from CaH_2. For anaerobic work, solvents (and solutions) were deoxygenated by passing a stream of argon through them for 15 min. Melting points are uncorrected.

Cyclic voltammetry (CV) was done with an EG&G Princeton Applied Research (PAR) Model 173 potentiostat/galvanostat, equipped with a Model 176 current follower, driven by a PAR Model 175 universal programmer. The voltammograms were recorded with a PAR Model RE0091 X-Y recorder. For measurements at 25 °C the temperature of the electrochemical cell was maintained by immersing it in a Neslab

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Endocal refrigerated circulating bath; a constant temperature of −44 °C was maintained by using a dry ice/CH_3CN slush bath.

The working electrode was a Pt button, and the counter electrode was a Pt coil. An $Ag/AgNO_3$ reference electrode was used; it consisted of a silver wire immersed in CH_3CN, 0.010 M in $AgNO_3$ and 0.09 M in TBAP. The reference electrode was separated from the bulk electrolyte by a Vycor plug (EG&G PAR, part no. G0100). The working and counter electrodes were activated by charging at +4.0 V (relative to the $Ag/AgNO_3$ reference electrode) for 15 s followed by 15 s at −4.0 V in bulk electrolyte solution. They were then rinsed with distilled H_2O, soaked in HNO_3 (concentrated) for 15 min, rinsed with distilled H_2O and methanol, and, finally, dried under vacuum.

The cell was assembled in the glovebox (under argon) for each measurement; the cell was closed off from the atmosphere during the actual measurement. Measurements were run on 2.5–11 mM solutions of the compound of interest in 5.0 mL of 0.10 M tetrabutylammonium perchlorate (TBAP) in CH_3CN. An oxidation was considered to be reversible if the oxidation half-wave, E_{ox}, and the reduction half-wave were the same size and shape and if $E_{ox} - E_{red} \sim 80$ mV (the value of $E_{ox} - E_{red}$ for E_1 and E_2, as measured with our electrochemical setup, of TMPD, which was known[31] to undergo two reversible oxidations).

The oxidation potentials given are the mean values of many measurements on single samples. From sample to sample of a particular compound, a difference between the mean values of greater than 10 mV was never observed; the standard deviation of the means, reported as the error, was therefore estimated to be ±10 mV.

1,3,5-Triamino-2,4,6-trinitrobenzene (11). Compound **11** was prepared with a procedure similar to that used by Backer and van der Baan.[21] The yield of **11** was 13.19 g (65%): mp >350 °C (lit.[21] mp >300 °C); IR (KBr) 3320 cm^{-1} (m), 3225 (m), 1585 (d, m), 1450 (m), 1220 (s), 1175 (s), 1030 (w), 785 (w), 730 (w), 700 (w).

Hexaaminobenzene (12). In a 0.5-L medium-pressure hydrogenation reaction vessel were suspended 2.5 g (9.7 mmol) of insoluble **11** and 0.6 g of 10% Pd on carbon in 60 mL of ethyl acetate, and the mixture was hydrogenated with 60 psi H_2 until the H_2 pressure remained nearly constant with time. The solvent was removed under reduced pressure, leaving a black powder. The crude hexaaminobenzene **12** was used without purification and as quickly as possible, because it decomposed rapidly even when stored under vacuum or argon.

Hexakis(chloroacetamido)benzene (13). K_2HPO_4 (40.0 g, 0.230 mol) was dissolved in 400 mL of distilled H_2O, and the resultant mixture was deoxygenated by purging with argon. Crude product mixture **12** from the reduction of 9.92 mmol of **11** was dissolved in this solution with stirring over a period of 10 min, and the catalyst was removed by filtration. While a slow stream of argon was passed continuously through the filtrate, 10.0 mL (0.126 mol) of chloroacetyl chloride was added dropwise to the solution with vigorous stirring. The reaction mixture was gently warmed to 40–45 °C, and portionwise (ca. 2-mL) addition of chloroacetyl chloride was continued until an additional 30.0 mL (0.378 mol) had been added over a 1.5-h period.

The reaction mixture gradually turned orange, and the precipitate thickened as the addition progressed. The mixture was allowed to cool to room temperature with stirring for 0.5 h, and then the product was collected by vacuum filtration and washed with H_2O, methanol, and then acetone. The yield of hexakis(chloroacetamido)benzene **13** as a light brown powder was 2.307 g (37% based on the trinitro compound). Yields as high as 60% for the two steps were occasionally obtained in subsequent preparations of **13**. An analytically pure sample of **13** could be obtained by trituration in boiling acetonitrile and then diethyl ether, followed by drying under vacuum: mp >350 °C; NMR (DMSO-d_6) 9.52 (s, 6 H), 4.22 ppm (s, 12 H); IR (KBr) 3250 (m), 3030 (w), 1685 (s), 1525 (s), 1415 (w) cm^{-1}; MS (CI, methane): M^+ 627 (4), (M − 6HCl + 1) 409 (100), (M − 6HCl + 29) 437 (18). Anal. Calcd for $C_{18}H_{18}Cl_6N_6O_6$: C, 34.47; H, 2.89; N, 13.40; Cl, 33.92. Found: C, 34.37; H, 2.86; N, 13.51; Cl, 33.99.

Hexakis(lactam) 14. A flask equipped with a magnetic stirring bar and capped with a septum was charged with 25 mL of DMSO (dried over activated 4-Å sieves). With stirring, 1.14 g (1.8 mmol) of **13** was added to the reaction vessel. After **13** had dissolved, 27.0 mL (11.6 mmol, 6.4 equiv) of 0.43 M sodium ethoxide in ethanol was added in small increments over a period of 2 h. Stirring was continued for an additional 2 h. About 0.5 mL of acetic acid was added to the reaction mixture, and the product was collected by vacuum filtration and washed with ethanol and then acetone. The yield of the hexakis(lactam) **14** as a fine off-white powder was 0.550 g (75%). Yields as high as 84% were obtained occasionally in subsequent preparations: mp >350 °C; NMR (DMSO-d_6) 4.46 ppm (s); IR (KBr) 3005 (w), 2920 (w), 1680 (s), 1535 (s), 1360 (s), 1235 (m), 1070 (w), 980 (w), 780 (w) cm^{-1}; MS (CI, methane) (M + 1) 409 (100), (M + 29) 437 (20). Anal. Calcd for $C_{18}H_{12}N_6O_6$: C, 52.94; H, 2.96; N, 20.58. Anal. Calcd for $C_{18}H_{12}N_6O_6 \cdot H_2O$: C, 50.71, H, 3.31; N, 19.71. Found: C, 50.60; H, 3.42; N, 19.36.

Reaction of 13 with 2 equiv of Base. Compound **13** (200 mg, 0.319 mmol) was dissolved with stirring in 6 mL of DMSO (dried over activated 4-Å sieves). With stirring, 1.5 mL (0.645 mmol, 2 equiv) of 0.43 M sodium ethoxide in ethanol was added over a period of 30 min. A white precipitate formed during this time; it was collected by centrifugation and washed with H_2O, methanol, and, finally, ether. This solid was determined by NMR to be pure hexalactam **14** in a yield of 43 mg (33%, or 99% based on added ethoxide).

The original supernatant was poured into 100 mL of H_2O, and the greyish solid that precipitated was collected by centrifugation and washed with methanol and then ether. This solid was determined by NMR to be pure **13** (starting material) in a yield of 126 mg (63%, or 94% of the expected yield of unreacted starting material).

HOC (9). The reaction was carried out under anhydrous and anaerobic conditions. A 250-mL flask equipped with a magnetic stirring bar and a reflux condenser was charged with 2.20 g (5.4 mmol) of **14**, then 160 mL (160 mmol) of 1.0 M BH_3 in THF was added to the reaction vessel. The suspension was brought to reflux. After 72 h the solution became light yellow, and a fine precipitate was present. Taking care to exclude air, the remaining BH_3/THF was removed under reduced pressure, leaving an oily brown solid. Under argon, 80 mL of deoxygenated 6 N HCl was slowly added to destroy the borane–amine complex. The resulting suspension was warmed to about 70 °C with stirring until (about 15 min) it was transformed into a homogeneous solution.

After being cooled in an ice bath (solid precipitate), the solution was neutralized with 80 mL of deoxygenated 6 N NaOH solution. At the point of neutralization, the solution became milky. An additional 10 mL of deoxygenated 6 N NaOH was added to the milky solution, which caused the precipitation of a large quantity of an off-white solid. The precipitate was collected by vacuum filtration under a positive pressure of argon and washed with three 5-mL portions of deoxygenated H_2O followed by two 5-mL portions of deoxygenated acetone. The yield of HOC (**9**) as an off-white powder was 1.04 g (59%). Yields as high as 80% were obtained on occasion. HOC is slightly water soluble, so anaerobic extractive workup of the filtrate with CH_2Cl_2 at times gave an additional 20% yield of HOC as a dark brown solid after removal of the solvent under reduced pressure. Analytically pure samples of HOC could be obtained by sublimation at 200 °C under a pressure of less than 20 μmHg: mp 274–277 °C (darkens above 240 °C); NMR ($CDCl_3$) 3.1 ppm (s, br), addition of I_2 (<$^1/_2$ equiv) wipes out the signal; IR (KBr) 2922 (m), 2887 (m), 2185 (s), 2756 (w), 1502 (s), 1452 (m), 1345 (s), 1298 (s), 1236 (s), 1185 (s), 1139 (m), 1102 (w), 906 (w), 855 (w), 642 (w) cm^{-1}; MS (EI) M^+ 324 (100), M^{2+} 162 (9). Anal. Calcd for $C_{18}H_{24}N_6$: C, 66.64; H, 7.46; N, 25.90. Found: C, 66.42; H, 7.57; N, 25.94.

HOC^+I^-. This preparation was carried out in the glovebox, and solvents were oxygen- and water-free. Crude HOC (125 mg, 0.385 mmol) was dissolved with stirring for 0.5 h in 45 mL of THF, and the solution was filtered to remove any insoluble matter. With stirring, 1.8 mL (0.173 mmol, 0.93 equiv of oxidant) of 0.096 M I_2 in CH_2Cl_2 was added dropwise to the pale yellow filtrate over a 10-min period. A flat-green solid separated from solution as the addition progressed. The suspension was allowed to stir for 0.5 h. After the addition was complete, the solid was collected by vacuum filtration and washed with two 5-mL portions of CH_2Cl_2/ethanol (1:1). The yield of HOC^+I^- as a flat-green powder was 134 mg (77% yield based on HOC, or 86% based on added oxidant): UV–vis (CH_3CN) 716 nm (ε 12 600), 378 (sh, 9800), 350 (10 300), 308 (26 700), 251 (31 000). Anal. Calcd for $C_{18}H_{24}N_6I$: C, 47.90; H, 5.36; N, 18.62. Anal. Calcd for $C_{18}H_{24}N_6I \cdot 0.5H_2O$: C, 46.96; H, 5.47; N, 18.25. Found: C, 47.27; H, 5.39; N, 18.03.

$HOC^+BPh_4^-$. This preparation was carried out in the glovebox. The solvents were oxygen- and water-free. Freshly sublimed HOC (111.2 mg, 0.343 mmol) was dissolved with stirring in 15 mL of CH_2Cl_2, and the solution was diluted with 45 mL of ethanol. $NaBPh_4$ (150 mg, 0.44 mmol) was added, and 3.20 mL (0.164 mmol, 0.96 equiv of oxidant) of 0.0512 M I_2 in ethanol was added dropwise to the filtered reaction mixture with stirring over 5 min. As the oxidant was added, the product was seen to precipitate. The suspension was allowed to stir for 15 min after the I_2 addition was complete, and then the grass-green solid was collected by vacuum filtration and washed with four 2-mL portions of ethanol. The yield of salt was 0.1938 g (88% from HOC, or 92% based on added oxidant). An analytical sample was prepared by drying at 39 °C under vacuum (20 μmHg) over P_2O_5 for 20 h: UV–vis (CH_3CN) 716 nm (ε 10 400), 373 (sh, 8300), 348 (8600), 304 (26 500). Anal. Calcd for $C_{42}H_{44}N_6B$: C, 78.37; H, 6.89; N, 13.06. Anal. Calcd for $C_{42}H_{44}N_6B \cdot C_2H_6O$: C, 76.62; H, 7.30; N, 12.18. Found: C, 77.40; H, 7.08; N, 12.52.

$HOC^+SbF_6^-$. This preparation was done in the glovebox. The solvents used were oxygen- and water-free. HOC (122.0 mg, 0.377 mmol) was suspended in 20 mL of CH_3CN (distilled from $KMnO_4$, and then CaH_2), and 1.1 mL (0.43 mmol, 1.1 equiv) of 0.39 M $NO^+SbF_6^-$ in CH_3CN was added dropwise to the HOC suspension over a 0.5-h period. THF (39 mL) was added to the resulting blue-green solution, and the volume of the THF/CH_3CN was reduced by half by vacuum evaporation. A small amount of solid separated from the solution and was removed by filtration. The filtrate was further concentrated to 1 mL and then treated with 40 mL of THF. A voluminous solid precipitated; it was collected by vacuum filtration and washed with several portions of THF/CH_3CN (6:1). The yield of $HOC^+SbF_6^-$, as a blue-green powder, was 153 mg (72%): UV-vis (CH_3CN) 717 nm (ϵ 8900), 354 (sh, 8500), 304 (20 900). Anal. Calcd for $C_{18}H_{24}N_6SbF_6$: C, 38.59; H, 4.32; N, 15.00. Found: C, 38.43; H, 4.12; N, 14.81.

UV-Vis Scale Preparation of HOC Dication 35. Sample preparation was carried out under anhydrous and anaerobic conditions. $HOC^+BPh_4^-$ (1.3 mg, 2.02 μmol) was dissolved in 25.0 mL of CH_3CN, and a 2.0-mL portion of this solution (0.162 μmol of $HOC^+BPh_4^-$) was transferred to a quartz cuvette. To this solution of HOC cation radical was added 10 μL (0.083 μmol) of 8.25 mM Br_2 in CH_3CN. The resulting pink solution was agitated to ensure complete mixing, and the visible spectrum was measured: vis (CH_3CN) 523 nm (ϵ 14 600), 360 (sh), 316 (27 700).

ESR of HOC Dication 35 in CH_2Cl_2/CH_3CN. Sample preparation was carried out in the glovebox. HOC (5.0 mg, 15.4 μmol) was suspended in 0.6 mL of CH_2Cl_2. With vigorous stirring, 0.3 mL (33 μmol) of 0.11 M $NO^+SbF_6^-$ in CH_3CN was added dropwise to the suspension. As the first equivalent was added, the solution turned blue and gradually became homogeneous. As the solid equivalent was added, the solution became purple in color and remained homogeneous. Half of this solution was withdrawn and placed in a quartz ESR tube. When frozen, this sample exhibited a very weak triplet signal. An excess of oxidant, 0.1 mL (11 μmol) of 0.11 M $NO^+SbF_6^-$ in CH_3CN, was added to the remaining solution of oxidized HOC; the solution became very dark purple. This solution, ca. 1.4×10^{-2} M HOC dication in CH_2Cl_2/CH_3CN (1.2:1), exhibited a strong triplet signal when frozen at 112 K (see Figure 2).

The intensity of the $\Delta m = 2$ line was measured at four different temperatures between 109 and 156 K (Figure 3). The signal did not lose any intensity when the sample was kept at room temperature for 3 h (sealed from the atmosphere with a rubber septum) and then refrozen. The sample still exhibited a triplet signal after being kept at room temperature for 24 h, but the signal was less intense: line positions ($\sigma = \pm 10$ G) 1580 G ($\Delta_m = 2$), 2640 and 3900 G (*z* lines), 2936 and 3558 G (*xy* lines); temperature (Δm = 2-line intensity in cm) 156 (14.2), 109 (19.6), 109 (19.2), 127 (16.6), 127 (16.6), 153 (14.0), 153 K (13.9).

ESR of HOC Dication 35 in CH_3CN. Sample preparation was carried out in the glovebox. HOC (5.4 mg, 16.6 μmol) was suspended in 0.60 mL of CH_3CN. With vigorous stirring, 0.340 mL (0.0334 mmol) of 0.0982 M $NO^+SbF_6^-$ in CH_3CN was added dropwise. As the first equivalent was added, the solution turned blue and became homogeneous. The solution became red-purple as the second equivalent of oxidant was added, and it remained homogeneous. After the addition was complete, the solution was pumped on for 1 min. The resulting red-purple solution, 1.8×10^{-2} M HOC dication in CH_3CN, was placed in a quartz ESR tube sealed with a pressure cap.

The frozen solution (155 K) exhibited a strong triplet signal. The intensity of the $\Delta m = 2$ line was measured at five different temperatures between 117 and 163 K (Figure 4): line positions ($\sigma = \pm 10$ G) 1562 G ($\Delta m = 2$ line); 2640 and 3820 G (*z* lines), 2900 and 3500 G (*xy* lines); temperature (Δm = 2-line intensity in cm) 156 (16.1), 142 (11.8), 129 (10.0), 117 (8.0), 163 K (16.9).

$HOC^{2+}(I_3^-)_2$. This preparation was carried out in the glovebox. HOC^+I^- (51.5 mg, 0.114 mmol) was dissolved in 50 mL of ethanol with stirring. The resulting blue solution was slowly added, with vigorous stirring, to 5.1 mL (0.325 mmol) of 0.0637 M I_2 in ethanol. A brown-red solid was observed to precipiate from solution as the reaction progressed. The reaction mixture was stirred for 15 min after the addition was complete. The product was collected by vacuum filtration and washed with ethanol. The yield of $HOC^{2+}(I_3^-)_2$ was 123.9 mg (100%): vis (CH_3CN) 525 nm (ϵ 10 500). Anal. Calcd for $C_{18}H_{24}N_6I_6$: C, 19.91; H, 2.23; N, 7.74; I, 70.12. Found: C, 19.93; H, 2.09; N, 7.47; I, 70.04.

ESR of $HOC^{2+}(I_3^-)_2$ in DMSO. The sample was prepared in the glovebox. $HOC^+(I_3^-)_2$ (15.7 mg, 14.5 μmol) was dissolved in 0.5 mL of deoxygenated DMSO to give a 2.9×10^{-2} M solution. The resulting red solution was transferred to a quartz ESR tube, which was capped with a pressure cap. When frozen, this sample did not exhibit a triplet signal in the temperature range 123–223 K.

Triaminophloroglucinol (18) Hydrogen Sulfate was prepared by the hydrogenation of trinitrophloroglucinol by a modification of the procedure reported by Quadbeck and Röhm[25] as a white powder, in 94% yield: mp 190–200 °C dec; IR (KBr) 3410 (w), 290 (s, br), 2625 (s), 1640 (m), 1595 (m), 1535 (m), 1500 (m), 1350 (m, br), 1205 (s), 1080 (d, s, br) 925 (w), 740 (w), 695 (w), 625 (w) cm^{-1}.

1,3,5-Tris(chloroacetamido)phloroglucinol (19). KH_2PO_4 (32.0 g, 0.235 mol) and 11.6 g (0.0666 mol) of K_2HPO_4 in 350 mL of distilled H_2O were deoxygenated by passing argon through the mixture for 0.5 h. Freshly prepared **18** (4.73 g, 14.9 mmol) was suspended in this solution, and over 15 min 25 mL (0.31 mol) of chloroacetyl chloride was added to the suspension with stirring. After 0.5 h, 3 mL (0.038 mol) more of chloroacetyl chloride was added with stirring; after an additional 15 min, 5 mL (0.063 mol) more of chloroacetyl chloride was added, and the reaction was cooled in an ice bath. The very light pink precipate that had formed was collected by filtration and washed with three 25-mL portions of H_2O. The yield of **19** was 5.15 g (86%). An analytically pure sample was obtained by recrystallization from toluene followed by drying at 111 °C under vacuum (20 μmHg) for 12 h: mp 225–227 °C dec; NMR (DMSO-d_6) 9.197 (s, 3 H), 8.886 (s, 3 H), 4.253 ppm (s, 6 H); IR (KBr) 3350 (m), 3330 (m), 3030 (w), 2960 (w), 2540 (m, br), 1650 (s), 1560 (s), 1480 (m), 1380 (s), 1300 (w), 1270 (m), 1140 (m), 1040 (m), 920 (m), 780 (s), 680 (m) cm^{-1}. Anal. Calcd for $C_{12}H_{12}Cl_3N_3O_6$: C, 35.98; H, 3.02; Cl, 26.55; N, 10.49. Found: C, 36.14; H, 3.04; Cl, 26.62; N, 10.36.

Cyclization to the O_3N_3 Tris(lactam) 17. 1,3,5-Tris(chloroacetamido)phloroglucinol (**19**; 0.6364 g, 1.59 mmol) was dissolved in 35 mL of 10% aqueous K_2CO_3 with stirring, and the solution was gently heated to ca. 40 °C for 0.5 h. The reaction mixture was cooled in an ice bath, and the precipitate was collected by vacuum filtration. The yield of tris(lactam) **17** as a white powder was 0.1616 g (35%). An analytically pure sample was obtained by recrystallization from ethylene glycol, followed by washing with methanol and drying at 111 °C under vacuum (20 μmHg) over P_2O_5 for 48 h: mp >350 °C; NMR (DMSO-d_6) 10.428 (s, 3 H), 4.493 ppm (S, 6 H); IR (KBr) 3170 (w, br), 1680 (s), 1530 (m), 1400 (w, br), 1175 (w), 1085 (m) cm^{-1}. Anal. Calcd for $C_{12}H_9N_3O_6$: C, 49.49; H, 3.12; N, 14.43. Found: C, 49.12; H, 3.36; N, 14.28.

Acidification of the filtrate with concentrated HCl resulted in the precipitation of a light pink solid, identified as the bis(lactam) **20**, in 0.243-g (47%) yield. An analytical sample was obtained by recrystallization from acetic acid, followed by washing with H_2O and methanol and then drying at 111 °C under vacuum (20 μmHg) over P_2O_5 for 18 h: mp 295–305 °C dec; NMR (DMSO-d_6) 10.12 (s, 2 H), 9.72 (s, 1 H), 9.47 (s, 1 H), 4.39 (s, 4 H), 4.23 ppm (s, 2 H); IR (KBr) 3480 (m), 3210 (m), 3080 (w), 1670 (s), 1555 (m), 1490 (m), 1455 (m), 1390 (m), 1265 (w), 1175 (m), 1135 (w), 1075 (m), 1030 (m), 1000 (w), 900 (m), 825 (w), 785 (w), 680 (w), 640 (w) cm^{-1}; MS (CI, NH_3) (M + 1) 328 (100); (M + 3) 330 (42), (M + 18) 345 (94), (M + 20) 347 (43). Anal. Calcd for $C_{12}H_{10}ClN_3O_6$: C, 43.99; H, 3.08; Cl, 10.82; N, 12.82. Found: C, 43.39; H, 3.63; Cl, 10.23; N, 12.57.

Methylation of the Tris(lactam) 17 to form 21. The tris(lactam) **17** (1.143 g, 3.92 mmol) was dissolved in 55 mL of DMSO (dried over activated 4-Å molecular sieves) with stirring. To the resulting solution was added 13.5 mL (12.2 mmol) of 0.90 M sodium ethoxide in ethanol. The suspension was stirred for 0.5 h, and then 8.3 mL (0.13 mol) of methyl iodide was added; the solution clarified almost immediately. After the resultant mixture was stirred for 0.5 h, 130 mL of H_2O was added to quench the reaction. The white precipitate was collected by vacuum filtration and washed with three 10-mL portions of H_2O. The yield of the product **21** as an off-white solid was 1.123 g (86%). An analytically pure sample was purified by flash chromatography with methanol/CH_2Cl_2 (7.7:92.3) as the eluent. The analytical sample was then dried at 111 °C under vacuum (50 μmHg) over P_2O_5 for 36 h: mp (crystallized from methanol/CH_2Cl_2) 272–273 °C; NMR (acetone-d_6) 4.588 (s, 6 H), 3.386 ppm (s, 9 H); IR (KBr) 3030 (w), 3000 (w), 2960 (w), 2930 (w), 1700 (s), 1615 (w), 1495 (w), 1460 (w), 1420 (w), 1375 (m), 1340 (w), 1110 (m), 1015 (w), 960 (w) cm^{-1}; MS (CI, NH_3) (M + 1) 334 (100), (M + 2) 335 (75), (M + 18) 351 (65), (M + 19) 352 (52). Anal. Calcd for $C_{15}H_{15}N_3O_6$: C, 54.06; H, 4.54; N, 12.61. Found: C, 53.87; H, 4.54; N, 12.36.

BONM (23). Tris(lactam) **21** (1.0273 g, 3.082 mmol) was suspended in 70 mL (70 mmol) of 1.0 M BH_3 in THF, and the suspension was heated under reflux for 2 h. The excess BH_3/THF was removed under reduced pressure, and the oily white residue was dissolved in 125 mL of 6 N HCl and warmed to 50 °C for 0.5 h. After being cooled, it was washed in a separatory funnel with three 75-mL portions of CH_2Cl_2. The solution was then neutralized with 6 N NaOH while it was cooled in an ice bath. The resulting turbid solution was extracted with three 60-mL portions of CH_2Cl_2, and the organic extracts were combined and washed with two 75-mL portions of saturated NaCl solution. Drying of the organic phase followed by removal of the solvent left an air-stable brown solid. Flash chromatography with methanol/CH_2Cl_2 (11:89) as the eluent gave 0.836 g (93%) of BONM (**23**) as an off-white powder. An analytically pure sample was prepared by drying chromatographed material at 77 °C under vacuum (100 μmHg) over KOH for 36 h: mp 148–150 °C; NMR ($CDCl_3$) 4.211 (t, J = 4.4 Hz, 6 H), 3.117 (t, J = 4.4 Hz, 6 H), 2.787 ppm (s, 9 H); IR (KBr) 2950 (w), 2880 (w), 2710 (w), 1600 (w), 1480 (m), 1450 (m), 1230 (m), 1150 (m), 1125 (m), 1075 (s), 990 (m), 920 (m), 880 (w), 810 (w) cm^{-1}. Anal. Calcd for $C_{15}H_{21}N_3O_3$: C, 61.84; H, 7.27; N, 14.42. Found: C, 61.65; H, 6.99; N, 14.37.

ESR Sample of $BONM^+I^-$. This preparation was performed in the glovebox. BONM (**23**; 6.5 mg, 22 μmol) was dissolved in 3.0 mL of deoxygenated trifluoroethanol. With stirring, 0.34 mL (11 μmol, one oxidative equiv) of 33 mM I_2 in CH_2Cl_2 was added to this solution. The solution gradually acquired a blue-purple color as the addition of I_2 progressed. The best resolved ESR spectrum of BONM radical cation iodide was obtained when the initially obtained solution was diluted with 3.0 mL of deoxygenated trifluoroethanol. The optimal concentration of BONM cation radical was thus 3.5 mM in trifluoroethanol/CH_2Cl_2 (18:1).

Samples of BONM cation radical iodide, both inside the glovebox and outside (sealed from the atmosphere with a rubber septum), turned purple within 24 h. An ESR sample that had turned purple had a significantly less intense doublet signal then when it was freshly prepared (ca. 5% of the intensity of the original signal).

An aliquot of a freshly prepared ESR sample of BONM cation radical was diluted with trifluoroethanol to a concentration of $\sim 4 \times 10^{-5}$ M. The UV–vis spectrum of this solution was measured. The extinction coefficients (ϵ) reported are only approximate, because the sample appeared to be decomposing as its spectrum was measured: UV–vis (trifluoroethanol) 560 nm (ϵ 3000), 353 (6000), 328 (6000), 273 (12 000).

ESR Sample of $BONM^+SbF_6^-$. This preparation was carried out in the glovebox. BONM (1.4 mg, 4.8 μmol) was dissolved in 0.5 mL of CH_3CN. To this solution was added 0.16 mL (4.5 μmol, 0.93 equiv) of 27.9 mM tris(4-bromophenyl)amminium (Ar_3N^+) hexafluoroantimonate with stirring. After the addition was complete, the solution was blue in color (the Ar_3N^+ solution was blue also). The solution of BONM cation radical was diluted with 0.5 mL of trifluoroethanol. An aliquot of this 4 mM solution of $BONM^+SbF_6^-$ in trifluoroethanol/CH_3CN/CH_2Cl_2 (4:4:1) was transferred to an ESR sample tube. The ESR spectrum of this sample was identical with the one obtained for BONM cation radical iodide, but better resolved.

$BONM^+PF_6^-$. This operation was performed in the glovebox. BONM (103.5 mg, 355 μmol) was dissolved in 4.0 mL of CH_3CN. With stirring, 1.80 mL (320 μmol, 0.90 equiv) of 0.178 M $NO^+PF_6^-$ (Alfa) in CH_3CN was added to this solution. After the first drop of oxidant was added, the solution acquired a red tint. As the addition progressed, the color of the solution turned blue-purple. After the addition was complete, the CH_3CN was removed under reduced pressure. The red-brown residue was dissolved in 1 mL of CH_3CN; the addition of 10 mL of diethyl ether caused a maroon solid to precipitate. The product was collected by filtration and washed with diethyl ether/CH_3CN (10:1). The yield of $BONM^+PF_6^-$ was 122.1 mg (79%, or 87% based on added oxidant). Anal. Calcd for $C_{15}H_{21}N_3O_3PF_6$: C, 41.29; H, 4.85; N, 9.63; P, 7.10; F, 26.13. Found: C, 42.33; H, 5.15; N, 9.74; P, 6.24; F, 21.80. Calculated ratios: C/N = 4.29; C/H = 8.51; N/H = 1.99. Found (error calculated assuming $\sigma = \pm 0.30\%$ for each analysis): C/N = 4.35 ± 0.13; C/H = 8.22 ± 0.48; N/H = 1.89 ± 0.11.

ESR of BONM Dication 36. This preparation was carried out under anhydrous and anaerobic conditions. BONM (**23**; 23.6 mg, 81.0 μmol) was dissolved in 1.0 mL of CH_2Cl_2. This solution was cooled in a dry ice/acetone bath. With vigorous stirring, 0.300 mL (163 μmol) of 0.544 M $NO^+SbF_6^-$ in CH_3CN was added to this solution dropwise. The solution gradually acquired a blue-green color. After the second equivalent of oxidant was added, the solution was exposed to vacuum for 2 min. The solution acquired a deep purple color after this action.

About 0.3 mL of this 6.2×10^{-2} M solution of BONM dication in CH_2Cl_2/CH_3CN (10:3) was transferred via cannula under positive argon pressure to a quartz ESR tube, which was immersed in a dry ice/acetone bath. When frozen (118 K), the sample exhibited a weak but typical triplet signal. When the sample was kept at room temperature for 15 min, it became green-brown; this green-brown solution did not exhibit a triplet spectrum when refrozen (118 K).

The intensity of the $\Delta m = 2$ line was measured at five different temperatures between 104 and 165 K: line positions ($\sigma = \pm 10$ G) 1577 G ($\Delta m = 2$), 2678 and 3860 G (z lines), 2938 and 3528 G (xy lines); temperature (Δm = 2-line intensity in cm) 111 (8.6), 111 (8.8), 124 (7.5), 124 (7.5), 140 (5.3), 140 (5.8), 104 (9.4), 104 (9.3), 165 (5.7), 165 K (5.6).

BONH (22). The reaction was done under anhydrous and anaerobic conditions. Tris(lactam) **17** (0.3079 g, 1.057 mmol) was suspended in 10 mL (10 mmol) of 1.0 M BH_3 in THF, and the mixture was heated under reflux for 1 h. Taking care to exclude air, the excess BH_3/THF was removed under reduced pressure leaving a pink-brown solid. Under argon, the solid was dissolved in 6 mL of deoxygenated 6 N HCl by warming the solution to 50 °C for 0.5 h; the solution was cooled in an ice bath and then made basic by the addition of 8 mL of NaOH.

The white precipitate was collected by vacuum filtration under a positive pressure of argon and washed with three 2-mL portions of ice-cold, deoxygenated distilled H_2O. The yield of BONH (**22**) as a grey-white solid was 153 mg (58%). The filtrate and washings were combined and extracted with three 10-mL portions of deoxygenated CH_2Cl_2 under a positive pressure of argon. The extracts were combined, and then the solvent was removed under reduced pressure. The yield of light brown solid was 80.4 mg (31%). The product, either that collected by filtration or that obtained by anaerobic extraction, was purified portion-wise by sublimation at 170 °C under a pressure of 50 μmHg. The yield of analytically pure **22** obtained in this manner, as a mildly air-sensitive white solid, was 56%: mp 216–219 °C; NMR ($CDCl_3$) 4.23 (t, J = 4.5 Hz, 2 H), 3.54 (br s, 3 H), 3.36 ppm (t, J = 4.2 Hz, 6 H); IR (KBr) 3460 (m), 2955 (w), 2915 (m), 2860 (m), 1625 (w), 1505 (s), 1450 (w), 1415 (w), 1335 (s), 1255 (w), 1225 (w), 1120 (s), 1050 (w), 1010 (w), 965 (m), 915 (w), 845 (w), 795 (w), 695 (w) cm^{-1}. Anal. Calcd for $C_{12}H_{15}N_3O_3$: C, 57.82; H, 6.07; N, 16.86. Found: C, 58.02; H, 6.25; N, 16.79.

ESR Sample of $BONH^+Br^-$. The reaction was done under anaerobic and anhydrous conditions. BONH (**22**; 2.4 mg, 9.63 μmol) was dissolved in 1.0 mL of CH_3CN. With stirring, 0.060 mL (4.66 μmol, 1 oxidative equiv) of 77.6 mM Br_2 in CH_3CN was added to this solution. As the Br_2 was added, a blue solid was seen to precipitate almost instaneously. The reaction vessel was transferred to the glovebox, where the supernatant was removed first by pipet and then under vacuum. The blue solid that remained was dissolved in 0.5 mL of deoxygenated trifluoroethanol to give a deep blue solution.

The best resolved ESR spectrum of BONH cation radical bromide was obtained when this initial solution was diluted with 0.5 mL of deoxygenated trifluoroethanol; the optimal concentration for ESR study of BONH cation radical bromide in trifluoromethanol was thus 9.6 mM.

ESR Sample of $BONH^+I^-$. This preparation was performed in the glovebox. BONH (**22**; 4.9 mg, 19.7 μmol) was dissolved in 3.0 mL of trifluoroethanol. With stirring, 0.77 mL (9.7 μmol, 1 oxidative equiv) of 12.6 mM I_2 in CH_2Cl_2 was added to this solution. The solution gradually acquired a deep blue color as the addition progressed. The best resolved ESR spectrum of BONH cation radical iodide was obtained with this solution; the optimal concentration of BONH cation radical iodide for ESR study was thus 5.2 mM in trifluoroethanol/CH_2Cl_2 (4:1).

A solution of BONH cation radical kept in the glovebox remained deep blue over a 24-h period. The ESR spectrum of an aliquot of the solution that was kept in the glovebox for 24 h was as intense as that of an aliquot withdrawn from a freshly prepared solution of BONH cation radical. An ESR sample of BONH cation radical stored outside the glovebox (sealed from the atmosphere with a rubber septum) turned orange within 24 h. This orange sample had a significantly less intense doublet signal in the ESR then when it was freshly prepared (ca. 10% as intense as the original signal).

An aliquot of a freshly prepared ESR sample of BONH cation radical was diluted with trifluoroethanol to a concentration of $\sim 5 \times 10^{-5}$ M. The UV–vis spectrum of this solution was measured. The sample visibly changed color as the spectrum was measured, so the numbers reported for both λ_{max} and ϵ are approximate at best: UV–vis (trifluoroethanol) 498 nm (ϵ 3000), 370 (2000), 331 (10 000), 260 (8000).

1,3,5-Triamino-2,4,6-trithiocyanatobenzene (27). The procedure used was adapted from that reported by Grandolini and Martani.[29] Ammonium thiocyanate (3.5 g, 46 mmol) was dissolved in a solution of 1,3,5-triaminobenzene (7.3 mmol) in methanol. The resulting solution was purged with argon for 15 min and then maintained under a positive pressure of argon for the duration of the reaction. The reaction mixture was cooled in an ice bath, and a solution of 2.6 mL (22 mmol) of *N,N*-dichlorourethane in 8.0 mL of deoxygenated methanol was added dropwise with stirring to the reaction vessel over a period of 10 min. An off-white precipitate was observed to form as the addition progressed.

The reaction mixture was stirred in the ice bath for an additional 2 h and then diluted with 75 mL of 10% K_2CO_3 solution. After 5 min, the off-white precipitate was collected by vacuum filtration and washed with several portions of distilled H_2O. The yield of the off-white product **27** was 1.817 g (84%). The crude product was recrystallized from dioxane and dried at 111 °C under vacuum (50 μmHg) over P_2O_5 for 18 h to remove the dioxane of crystallization. The yield of tan crystals was 1.572 g (73% based on 1,3,5-trinitrobenzene, from which the 1,3,5-triaminobenzene was prepared by hydrogenation). A sample of **27** prepared in this manner was found to be analytically pure: mp 236 °C dec (lit.[29] mp 243–244 °C dec); IR (KBr) 3470 (s), 3350 (s), 3200 (w), 2155 (s), 1600 (s), 1525 (s), 1440, 1430 (m, d), 1040 (w), 750 (m), 660 (w) cm^{-1}. Anal.

Calcd for $C_9H_6N_6S_3$: C, 36.72; H, 2.05; N, 28.55. Found: C, 36.71; H, 2.17; N, 28.20.

The S_3N_3 Tris(lactam) 26 was prepared as reported by Grandolini and Martani.[29] The yield of crude product was 1.357 g. Analysis of the product mixture by NMR spectroscopy revealed it to be a ca. 1:1 mixture of the desired product **26** and the bis(lactam) **29**.

Recrystallization of the crude product mixture from ethylene glycol gave the tris(lactam) **26** as tan needles in 31% yield. Drying the product at 111 °C under vacuum (20 μmHg) over P_2O_5 for 12 h gave analytically pure material: mp >350 °C (lit.[29] mp >350 °C); NMR (DMSO-d_6) 9.980 (s, 3 H), 3.352 ppm (s, 6 H); IR (KBr) 3345 (w), 3220 (w, br), 2920 (w), 1675 (s), 1575 (m), 1460 (m), 1400 (w), 1355, 1335 (d, m), 695 (w) cm^{-1}. Anal. Calcd for $C_{12}H_9N_3O_3S_3$: C, 42.47; H, 2.67; N, 12.38; S, 28.34. Found: C, 42.41; H, 2.72; N, 12.21; S, 28.11.

Extraction of the crude product mixture with hot ethanol followed by cooling of the hot filtrate gave the bis(lactam) **29** in 29% yield as a light brown granular solid: mp 282–286 °C dec (lit.[29] mp 315 °C dec); NMR (DMF-d_7) 9.728 (s, 2 H), 5.659 (s, 2 H), 3.700 (s, 2 H), 3.554 ppm (s, 4 H); IR (KBr) 3415 (w), 3320 (m), 3215 (w), 3000 (w), 2920 (w), 1710 (s), 1675 (s), 1610 (s), 1515 (m), 1470 (m), 1430 (m), 1400 (m), 1335 (s), 1255 (m), 1145 (m), 900 (w), 660 (m) cm^{-1}; MS (CI, CH_4) (M + 1) 358 (78), (M + 3) 360 (10), (M + 18) 375 (100), (M + 20) 377 (17).

Conversion of the Bis(lactam) 29 to the Tris(lactam) 26. Compound **29** (36.2 mg, 0.10 mmol) was suspended in 20 mL of absolute ethanol. A trace (ca. 0.25 mL) of 1 N HCl was added to the reaction mixture, and it was brought to reflux. After 48 h, the reaction was cooled to room temperature, and the white precipitate was collected by vacuum filtration and washed with methanol. The yield of tris(lactam) **26**, judged to be pure by NMR, was 30.0 mg (88%).

Preparation of the Trimethylated S_3N_3 Tris(lactam) 31. Tris(lactam) **26** (0.325 g, 0.958 mmol) was dissolved in 20 mL of DMSO (dried over activated 4-Å molecular sieves). To this solution was added 3.90 mL (2.88 mmol) of 0.739 M sodium ethoxide in ethanol, the suspension was stirred for 1.5 h, and 0.6 mL (9.6 mmol) methyl iodide was added to the reaction mixture. The resulting clear solution was stirred for an additional 1 h, and then it was poured into 75 mL of distilled H_2O. The resulting suspension was cooled in an ice bath, and after 0.5 h the tan crystals were collected by vacuum filtration and washed with several portions of distilled H_2O. The yield was 0.327 g (89%). Samples were purified for elemental analysis by flash chromatography with CH_2Cl_2/methanol (97:3) as the eluent: mp >320 °C; NMR ($CDCl_3$) 3.394 (s, 3 H), 3.33 ppm (br, s, 2 H); IR (KBr) 3010 (w), 2945 (w), 1675 (s), 1535 (m), 1430 (w), 1395 (m), 1335 (s), 1255 (w), 1235 (w), 1215 (w), 1150 (w), 1095 (s), 995 (w), 900 (w, br), 885 (w), 775 (w), 720 (w), 695 (w), 650 (w) cm^{-1}; MS (CI, NH_3) (M + 1) 382 (60); (M + 3) 384 (11), (M + 18) 399 (100), (M + 2) 401 (17). Anal. Calcd for $C_{15}H_{15}N_3O_3S_3$: C, 47.23; H, 3.96; N, 11.01; S, 25.21. Found: C; 47.00, 47.83; H; 4.16, 4.06; N; 10.13, 10.90; S; 24.67.

BSNM (25). A reaction vessel was charged with 0.3124 g (0.819 mmol) of **31** and 12.0 mL (12.0 mmol) of 1 M BH_3 in THF. The resulting suspension was brought to reflux for 2 h. The excess BH_3/THF was then removed under reduced pressure, and the residue was dissolved with heating in 10 mL of 6 N HCl for 15–30 min at 60 °C. The solution was cooled in an ice bath and made basic by the addition of 15 mL of 6 N NaOH. A white precipitate was collected by vacuum filtration and washed with several portions of H_2O. The yield of crude BSNM (**25**) as an off-white powder was 0.226 g (81%). Purification by flash chromatography with CH_2Cl_2 as the eluent gave 0.169 g (61%) of **25**. A sample purified by flash chromatography was submitted for elemental analysis: mp 252–253 °C; NMR ($CDCl_3$) 3.228 (m, 2 H), 3.08 (m, 2 H), 2.689 ppm (s, 3 H); IR (KBr) 2940 (d, m), 2870 (d, w), 2820 (w), 1380 (s), 1360 (w), 1265 (w), 1215 (m), 1185 (w), 1120 (w), 1100 (m), 1050 (m), 950 (w), 830 (m), 730 (m) cm^{-1}; MS (CI, NH_3) (M + 1) 340 (100), (M + 3) 342 (17). Anal. Calcd for $C_{15}H_{21}N_3S_3$: C, 53.06; H, 6.23; N, 12.38. Found: C, 52.96; H, 6.75; N, 12.73.

Oxidation of this species with $NO^+SbF_6^-$ produced a cation radical with a broad ESR signal. No triplet ESR signal could be seen with an excess of the oxidant.

BSNH (24). A reaction vessel was charged with 49.5 mg (0.146 mmol) of tris(lactam) **26** and 4.0 mL (4.0 mmol) of 1 M BH_3 in THF. The suspension was brought to reflux for 2 h, and the excess BH_3/THF was removed under reduced pressure leaving a yellow solid. The residue was taken up in 6 mL of 6 N HCl and the solution was warmed to 60 °C for 15 min. It was then cooled in an ice bath and made basic by the addition of 7 mL of 6 N NaOH. An off-white precipitate formed; after being stirred for 15 min in the ice bath, it was collected by vacuum filtration and washed with several portions of H_2O. The yield of crude BSNH (**24**) was 36.3 mg (84%). Purification by flash chromatography with CH_2Cl_2/methanol (98:2) as the eluent and with argon pressure gave 30.9 mg (71%) of **24** as an off-white solid: mp 202–204 °C; NMR ($CDCl_3$) 4.170 (br s, 1 H), 3.697 (m, 2 H), 2.931 ppm (m, 2 H); IR (KBr) 3380 (w), 2920 (w), 2860 (w), 1565 (s), 1490 (m), 1450 (w), 1410 (w), 1375 (w), 1330 (m), 1285 (w), 1215 (w), 1155 (w) cm^{-1}; MS (CI, NH_3) (M + 1) 298 (100), (M + 3) 300 (47).

Treatment of this material with I_2 led to a poorly defined doublet ESR signal. No triplet ESR spectrum could be elicited under various oxidizing conditions.

Acknowledgment. This work was supported by a grant from the U.S. National Science Foundation.

N,*N'*-Dibenzyl-*N*,*N'*-ethylenetartramide: A Rationally Designed Chiral Auxiliary for the Allylboration Reaction

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Abstract: The chiral auxiliary designated in the title was designed as a probe of our previously suggested mechanism of asymmetric induction with tartrate allylboronates **1–3**, namely that n/n electronic repulsive interactions between electron pairs on the aldehydic oxygen atom and an ester carbonyl disfavor transition-state C relative to A. The results reported for the new reagent **5** strongly support this thesis and suggest that the convergence of functional groups toward a metal center can be an exceedingly useful strategy for achieving a topological bias in the enantioselective functionalization of a carbonyl group.

Recent publications from several laboratories have demonstrated the potential of the allylboration reaction as a method for acyclic diastereoselective synthesis.[2,3] We have concentrated on tartrate allylboronates **1–3** and have shown that good to excellent stereoselectivity is obtained with a range of chiral and achiral aldehydes (typically 60–88% ee). While this level of stereoselection

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[1] On leave from the Università di Genova, Italy and recipient of a grant from the Consiglio Nazionale delle Ricerche.

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