reduces the negative charge on the carbanionic carbon atom by approximately 0.08 electron.

Although gas-phase acidities do not appear to be available for isocyanides, estimates of these can be made from the present work. The calculated gas-phase acidity ($\Delta H°$) for CH_4 (560.0 kcal/mol) reduced by the stabilization energies given in Table II will correspond to the gas-phase acidities of the neutral isocyanide molecules. The same information can be employed to assess the effects of methyl substitution. Addition of a first and a second methyl group reduces $\Delta H°$ (acid) by 6.1 and 1.7 kcal/mol, respectively.

Periasamy and Walborsky[4] have noted that when the carbanionic center is an asymmetric carbon, the configurational stability of the carbanion can then be measured. Hence the cyclopropyl anion system is appropriate for experimental study. Furthermore, the strain energy of approximately 26 kcal/mol which is associated with the cyclopropane ring[6] would be increased during the process of inversion, thus producing an intrinsic energy barrier to pyramidal inversion. Substituent effects can also be conveniently examined.

The geometries reported in the present work provide evidence for the relative unimportance of resonance delocalization in the isocyano carbanions studied. It has been pointed out by Periasamy and Walborsky (PW)[4] that resonance stabilization would be favored by a planar configuration in the substituted carbanion, while inductive effects should be favored by a pyramidal geometry. Further, PW[4] conclude that with (1-isocyano-2,2-diphenylcyclopropyl)lithium (IDCL), the α-isocyano carbanion favors a pyramidal configuration. Although the species examined in the present work are much less complex than that considered by PW, some comparisons appear to be valid. The present results appear to support those of PW in respect of the expectation of a pyramidal geometry for isocyanosubstituted carbanions. Further, the calculated distribution of charge from the present work lends support to their argument that the isocyano group does not act as a delocalizing substituent but as an electron-withdrawing group operating largely through an inductive effect.[4]

Although minimal basis set data cannot be expected to produce absolute electronic energies, nevertheless it is anticipated that calculated nuclear configurations will be reasonably accurate. It has been noted[7,8] that the small amount of experimental structural data which is available for anions appears to be adequately reproduced by molecular orbital calculations at the minimal basis set STO-3G level. Further it is now well documented that such a basis set is capable of reproducing the known geometrical structures for a wide variety of neutral species.[9] In addition, the use of isodesmic reactions will provide at least a partial cancellation of errors due to neglect of electron correlation and limitations in the basis set.[10]

The present calculations are applicable to the free carbanion and do not include any consideration of the effects of interactions between the charged species or with a solvent. It has been pointed out[11] that the geometry of the carbanion depends on the nature of the ion pair in solution. However Periasamy and Walborsky[4] have demonstrated that, with IDCL, the anion is capable of retaining its configuration whether it exists as a contact ion pair, solvent separated ion pair, or a free ion pair. Consequently it may be expected that the introduction of perturbing species would not alter the semiquantitative conclusions from the present work.

Acknowledgment. The financial assistance of the Natural Science and Engineering Research Council is gratefully acknowledged.

Registry No. CH_3NC, 593-75-9; CH_2NC^+, 78269-43-9; CH_2NC^-, 81704-80-5; CH_3^-, 15194-58-8; C_2H_5NC, 624-79-3; $C_2H_4NC^+$, 78269-44-0; $C_2H_4NC^-$, 81704-81-6; $C_2H_5^-$, 25013-41-6; C_3H_7NC, 598-45-8; $C_3H_6NC^+$, 78269-45-1; $C_3H_6NC^-$, 81704-82-7; $C_3H_7^-$, 25012-80-0.

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Stereochemistry of *trans*-1,4,5,8-Tetranitroso-1,4,5,8-tetraazadecalin: An Attractive Interaction between Peri Nitroso Groups

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Contribution from the Research Department—Code 3853, Naval Weapons Center, China Lake, California 93555, and Nicolet Magnetics, Inc., Mountain View, California 94041.
Received December 3, 1981

Abstract: The preferred configuration of *trans*-1,4,5,8-tetranitroso-1,4,5,5-tetraazadecalin, **3**, is the anti,syn,anti,syn configuration, **3c**, with S_2 symmetry. It is more stable than the anti,anti,anti,syn configuration, **3d**, by approximately 1.5 kcal/mol, and the anti,anti,syn,syn and anti,anti,anti,anti configurations, **3b** and **3a**, by approximately 3.0 kcal/mol. These results were established on the basis of the ^1H and ^{15}N NMR spectra of **3**. The relative stability of **3a-d** and the ^{15}N NMR chemical shifts in **3a-d** have been rationalized on the basis of a bonding interaction between the oxygen of a syn nitroso group and the adjacent nitroso nitrogen in a 1,8- or 4,5-syn,anti configuration plus a strong destabilizing electrostatic interaction that occurs in the anti,anti,syn,syn configuration because two partial positive charges are placed in close proximity.

It is well-established that the nitrosamino group is planar and that there is restricted rotation about the N-N bond due to its partial double bond character.[1] In *N,N*-dimethylnitrosamine this barrier has been measured to be 23 kcal/mol.[2] Dinitrosamines such as *N,N*-dinitrosopiperazine, **1**, exist as cis and trans isomers corresponding to the two possible relative arrangements of the nitroso groups.[3] The cis:trans ratio in this case has been de-

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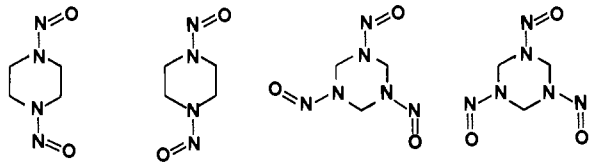
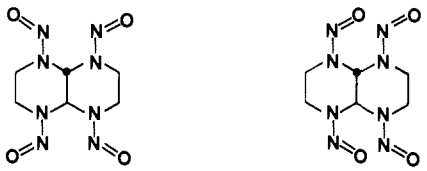


1a 1b 2a 2b

termined to be approximately 40:60 by ^{1}H NMR spectroscopy. The related 1,3,5-trinitroso-1,3,5-hexahydrotriazine, **2**, exists as a roughly statistical mixture (1:2) of the symmetrical (**2a**) and unsymmetrical (**2b**) forms.[4] The isomer ratios in **1** and **2** clearly establish that there is little, if any, electronic interaction between the nitrosamine functions in these compounds.

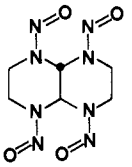
Results

We recently synthesized[5] the related compound *trans*-1,4,5,8-tetranitroso-1,4,5,8-tetrazaadecalin, **3**, by treating the known[6] *trans*-1,4,5,8-tetraazadecalin with nitrous acid. This compound could exist as four isomers, with the nitroso groups oriented as shown.

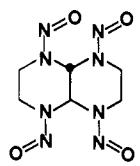


3a anti,anti,anti,anti

3b anti,anti,syn,syn



3c anti,syn,anti,syn

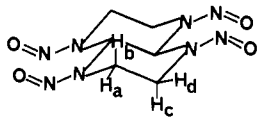


3d anti,anti,anti,syn

We have chosen to designate the stereochemistry of the nitroso group with respect to the bridgehead carbons. Syn refers to the configuration in which the oxygen of the nitroso groups points toward the bridgehead carbon, and anti refers to the configuration in which the oxygen of the nitroso group points away from the bridgehead carbon.

We have established that **3** exists in Me_2SO solution as an 88:12:0.5 mixture of **3c**, **3d**, and **3a**, respectively, on the basis of its ^{1}H NMR spectrum. We have also probed the reason for this preference using ^{15}N and ^{13}C NMR spectroscopy and in the process have found evidence for the fourth possible isomer, **3b**. Our assignment of structure rests upon the predicted ^{1}H NMR spectra for the ethylene fragments and bridgehead protons in **3a–d**. Summarized in Table I are the point group symmetries of **3a–d**, the type of spin system that the ethylene fragments and bridgehead protons form, and the statistical weight of each isomer.[7] It is easily seen that each possible isomer has an unique predicted ^{1}H NMR spectrum.

The 360-MHz ^{1}H NMR spectrum of **3** in Me_2SO-d_6 consists of two sets of overlapping spectra, one nearly ten times more intense than the other. The intense spectrum consists of a singlet at 6.73 ppm and multiplets at approximately 5.5, 4.9, and 3.9 ppm, with an integrated intensity ratio of 1:1:1:2. The series of multiplets is easily analyzed as an ABCD-type spin system. This clearly establishes that the intense spectrum belongs to isomer **3c**. We have simulated this part of the spectrum using the LAOCOON program[8] and have refined the spectral assignments to a root mean square error of 0.17 Hz. The resulting chemical shifts and coupling constants are summarized below. The assignments



$\nu_a = 5.52$ ppm, $J_{ab} = -14.72$ Hz
$\nu_b = 4.92$ ppm, $J_{ac} = 5.75$ Hz
$\nu_c = 3.95$ ppm, $J_{ad} = 1.03$ Hz
$\nu_d = 3.90$ ppm, $J_{bc} = 13.25$ Hz
$J_{bd} = 4.02$ Hz
$J_{cd} = -14.57$ Hz

are based upon the known greater downfield shift of protons anti to the nitroso oxygen[9] and the magnitude of the coupling constants. The torsional angle of the ethylene fragment can be calculated from the pertinent coupling constants by the *R*-value method to be 52°.[10] This is consistent with a six-membered ring that is flattened due to the incorporation of two trigonal nitrogens.

The weaker subspectrum consists of two doublets at 6.85 and 7.75 ppm and multiplets at 5.65, 5.30, 4.10, and 3.70 ppm. The appearance of the bridgehead protons as a pair of doublets clearly establishes the weaker subspectrum as belonging to isomer **3d**. This is further confirmed by the fact that the multiplets at 5.65, 5.30, and 4.10 ppm can by analyzed as an ABCD spin system, with coupling constants essentially identical with the ones found for isomer **3c**. The multiplet at 3.70 ppm is extremely complex but appears to be another ABCD spin system, but with much small shift differences. Careful integration of the signals for the bridgehead protons gives an isomer ratio of 88:12 (**3c**/**3d**).

Since **3d** is statistically favored 2:1 over **3c**, the 88:12 isomer ratio corresponds to a conformational energy difference (ΔH^{298}) of 1.59 kcal/mol. Since this energy difference between **3c** and **3d** would appear to be due to some type of attractive interaction between the oxygen of the *syn*-nitrosamine group and the adjacent nitroso nitrogen, one would predict that isomer **3a** would be twice

Table I. Predicted ^{1}H NMR Spectra for the Possible Isomers of **3**

	3a	3b	3c	3d
point group	C_{2h}	C_2	S_2	C_1
statistical weight	1	2	2	4
spin system(s), ethylene fragment(s)	AA'BB'	$A_1A_1'B_1B_1'$, $A_2A_2'B_2B_2'$	ABCD	$A_1B_1C_1D_1$, $A_2B_2C_2D_2$
spin system for bridgehead protons	A_2	A_2	A_2	AB

Table II. Nitroso Region of the ^{15}N NMR Spectrum of **3** in Me_2SO-d_6

isomer	chemical shifts, ppm[a]	rel intsty[b]
3a	543.2	1.6
3b	548.1, 542.8	0.8
3c	546.7, 532.6	100
3d	557.9, 547.4, 536.9, 533.0	6.0

[a] Downfield from liquid NH_3, 25 °C. [b] Based on relative peak heights.

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Figure 1. Possible interactions between peri nitroso groups.

as disfavored as **3d**, or 3.16 kcal/mol higher in energy than **3c**. This corresponds to an equilibrium constant K_{eq} = [**3a**]/[**3c**] of approximately 200. Indeed, in spectra with good signal/noise ratios, a singlet at 7.95 ppm with the proper intensity is observed, which we believe belongs to the bridgehead proton of **3a**. Unfortunately, the expected AA'BB' spectrum for the ethylene fragment of **3a** would be expected to appear near 3.80 ppm and therefore would be difficult to sort out from the signals for **3c** and **3d**, which appear in the same region. The spectrum did contain some additional weak multiplets that we could not assign. However, we could not find the expected singlet for the bridgehead protons of **3b**. It could, however, be coincident with the bridgehead protons for **3c**.

We next examined the ^{15}N NMR spectra of **3**. The poor solubility of **3** in all solvents prevented us from obtaining the ^{15}N NMR spectra at natural abundance, so **3** was synthesized with the nitroso nitrogens enriched to 95% ^{15}N with ^{15}N-labeled sodium nitrite. The ^{15}N NMR (36.6 MHz) spectrum of the nitroso region of **3** in Me_2SO-d_6 is summarized in Table II. As expected, the spectrum consists of two intense lines for isomer **3** and four less intense lines for isomer **3d**. In addition, a weak signal for isomer **3a** and a pair of weak lines for isomer **3b** were observed. The signals at 546.7 and 547.4 ppm are weakly coupled to protons (J_1 = 2.5 Hz, J_2 = 1.4 Hz), which allow them to be assigned to the syn nitroso groups in **3c** and **3d**, since it has been established that the nitroso nitrogen couples more strongly to methylene groups trans to the nitroso oxygen.[11] It is improtant to mention that the ^{15}N NMR spectrum of *N,N*-dinitrosopiperazine, **1**, in Me_2SO at natural abundance displays four signals, at 242.5 and 242.7 ppm for N_1 of the cis and trans isomers and 539.8 and 540.0 ppm for N_2 of the cis and trans isomers.[12]

The proton-decoupled ^{13}C NMR spectrum of **3** in Me_2SO-d_6 consists of three equally intense lines for **3c** at 43.95, 45.97, and 66.41 ppm. Poor solubility of **3** did not permit a sufficient signal/noise ratio to observe the signals for **3d**, **3a**, or **3b**. We have also obtained the proton-decoupled ^{13}C NMR spectrum of *N,N*-dinitrosopiperazine, **1**, for comparison. The cis isomer, **1a**, displays signals at 36.09 and 49.03 ppm, while the trans isomer displays signals at 43.95 and 46.13 ppm. The ^{13}C NMR results then only give further confirmation of our structural assignment for **3c**.

Discussion

The experimental results clearly establish that **3** exists in solution as an 88:12:0.5 mixture of isomers **3c**, **3d**, and **3a**, respectively, with perhaps as much **3b** present as there is **3a**. The seemingly close similarity of isomers **3b** and **3c** coupled with the known small energy difference between *cis*- and *trans*-*N,N*-dinitrosopiperazine makes the low population of **3b** quite remarkable. Just as remarkable is the great variation in chemical shifts of the nitroso nitrogen in **3a–d**, which span a range of 25 ppm. We believe that it is possible to formulate a rather simple explanation that accounts not only for the isomer distribution in **3** but also for the variation in chemical shifts of the nitroso nitrogens in **1**, **3a–d**.

It would be tempting to explain the fact that isomer **3c** is more stable than **3d**, which is in turn more stable than **3a**, by either an attractive interaction between the inner oxygen and the adjacent nitroso nitrogen in the syn,anti configuration, as shown in Figure 1a, or a repulsive interaction between the lone pairs on the nitroso nitrogen in the anit,anti configuration, as shown in Figure 1b. Neither of these explanations can be wholly correct. Both would predict that **3b** (which is only slightly populated) should be equal in energy to **3c**, the most stable isomer. One way to explain both

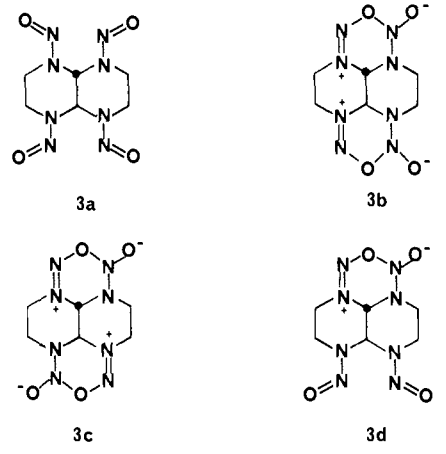
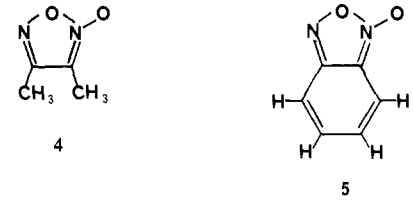


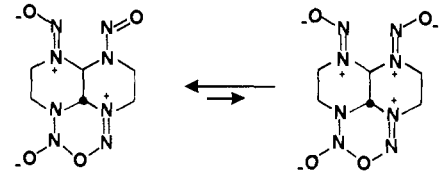
Figure 2. Possible isomers of **3** with weak bonding interactions shown.

the energy differences between **3c**, **3d**, and **3a** and the low population of **3b** is to postulate a weak bonding interaction between the syn oxygen and the adjacent nitroso nitrogen in the syn,anti configurations. Figure 2 shows isomers **3a–d** with this bonding interaction.

The energy differences between **3c**, **3d**, and **3a** are due to the fact that **3c** has two of these bonding interactions, **3d** has one, and **3a** has none. The cause of the much higher energy of **3b**, which has two of these stabilizing interactions, is the very unfavorable proximity of two positively charged nitrogens in the same ring. The appealing quality of this explanation is that it also accounts for the variations in the ^{15}N chemical shifts in **3a–d** and **1**. In **3c** there are two different nitroso groups. As already explained, the more downfield one can be assigned to the syn nitroso group, since it is spin-coupled to the adjacent methylene group. The shift difference (14 ppm) between the two nitroso groups is similar to the chemical shift difference noted for the two nitrogens in 3,4-dimethylfuroxane, **4** (12 ppm), and benzofuroxane, **5** (13.5 ppm), in which a similar type of bonding interaction occurs.[13] In **3d**, two of the four ^{15}N nitroso resonances



are virtually identical with those in **3c** and are easily assigned. The remaining two resonances are for the two anti,anti nitroso groups. The great difference in their shifts (536.9 and 557.9 ppm) is readily explained by the fact that one of them is across the ring from a positively charged nitrogen. This should greatly decrease the contribution from the resonance form, because of the unfavorable interaction between the two positive charges. Another



way of stating this is to say that the positive charge across the ring increases the contribution from the localized structure, which would be expected to have a shift more like that of C-nitroso compounds, which are shifted considerably downfield (nitrosobenzene = 913 ppm). The shifts of the nitroso nitrogens in **3a** and **1** are those typical of an unperturbed nitrosamine, since no

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interaction occurs in these molecules. The smaller shift difference between the two different nitroso nitrogen in **3b** as compared to **3c** (5.5 vs. 14.7 ppm) probably reflects the reduced amount of interaction between the syn nitro oxygen and anti nitroso nitrogen.

We believe that the foregoing explanation, based on the weak bonding interaction between the suitable juxtaposed nitrosamine groups, provides a conceptually simple and correct explanation for both the unusual isomer distribution observed in **3** and the large variation in chemical shifts of the nitroso nitrogen in **3a-d** and **1**.

Experimental Section

The NMR spectra were recorded on a Nicolet WB-360 MHz spectrometer. The ^1H and ^{13}C NMR spectra are referenced to internal Me_4Si. The ^{15}N NMR spectra are reported on the ammonia scale (NH_3 = 0 ppm). The reference standard was dimethylformamide; a conversion term of 103.81 ppm[14] was used to convert the data to the ammonia scale.

1,4,5,8-Tetranitroso-1,4,5,8-tetraazadecalin (3). A solution of 3.45 g (50 mmol) of sodium nitrite and 1.42 g (10 mol) of 1,4,5,8-tetraazadecalin was prepared in a 125-mL Erlenmeyer flask. The temperature of this solution was not allowed to exceed 5 °C. The solution was cooled to -2 °C, and 50 mL of 1 N hydrochloric acid was added over 60 s. A white precipitate formed immediately. The mixture was stirred at 0 °C for 30 min and then at room temperature for 1 h. The product was collected by vacuum filtration and was washed well with water. It was dried overnight in a vacuum oven to give an off-white powder (2.35 g, 9.1 mmol, 91%, decomposed at 211-212 °C). It was recrystallized from DMF/H_2O to yield fine light yellow neddles: IR (KBr) 2900 (w), 1475 (m), 1450 (sh), 1410 (m), 1370 (m), 1310 (m), 1300 (m), 1275 (m), 1260 (m), 1210 (m), 1190 (m), 1110 (m), 1050 (m), 975 (w), 935 (m), 895 (w), 830 (w), 735 (m); ^1H NMR Me_2SO-d_6, 80 °C) δ 3.80-4.10 (cm, 4 H), 4.95 (cm, 2 H), 5.55 (cm, 2 H), 6.76(s, 2 H, $H_{9,10}$). Anal. Calcd. for $C_6H_{10}N_8O_4$: C, 27.90; H, 3.91; N, 43.40. Found: C, 27.92; H, 3.91; N, 43.53.

The ^{15}N-labeled **3** was synthesized by substituting labeled sodium nitrite for the natural material in the preparation.

Registry No. 1, 140-79-4; *trans*-**3**, 81898-35-3; *trans*-1,4,5,8-tetraazadecalin, 67919-28-2.

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Inclusional Association of a Fluorescence Detergent Probe with Cyclodextrins. Microscopic Environment of the Interior of a Cyclodextrin Cavity. Pressure Effects

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Abstract: The fluorescence parameters (peak maximum, lifetime, relative intensity, and depolarization) of aqueous solutions of a cationic detergent probe, 11-(3-hexyl-1-indolyl)undecyltrimethylammonium bromide (6-In-11$^+$), have been measured in the presence of α-, β-, and γ-cyclodextrins (α-CD, β-CD, and γ-CD) at ambient and elevated pressures. The results are consistent with the formation of complexes of 6-In-11$^+$ and the CD's. NMR measurements confirm the existence of 6-In-11$^+$/CD complexes. It is concluded that the probe experiences a somewhat different environment in each complex. The results are compared to those for the same probe in the environment of ionic micelles and of the macroions of polyelectrolytes.

The properties of cyclodextrin (CD) inclusion complexes in aqueous solution have served as important models for the attainment of knowledge relevant to hydrophobic interactions, such as those that determine many of the critical properties of biological systems, i.e., the selectivity and catalytic efficiency of enzyme action.[2] Both the static and the dynamic properties of CD complexes may be investigated by means of luminescence probes.[3] The main goals of this work were to first determine the environmental polarity and mobility of a probe that is included in a CD cavity and then to establish how these properties vary as a function of applied pressure. A fluorescent detergent probe, 11-(3-hexyl-1-indolyl)undecyltrimethylammonium bromide (6-In-11$^+$), was selected because the values of $\lambda^F_{max} \sim 370$ nm and $\tau_F \sim 15$ ns are typical of a highly polar, aqueous environment and values of $\lambda^F_{max} \sim 350$ nm and $\tau_F \sim 7$ ns are typical of a less polar, hydrophobic environment.[5] Furthermore, the fluorescence depolarization of 6-In-11$^+$ affords a measure of the microviscosity of the environment experienced by the probe.[6]

In addition to the above points, the fact that 6-In-11$^+$ is at once a fluorescence probe and a detergent allows the examination of how a detergent structure can influence the binding to a CD,[7] and finally, the effect of applied pressure on the luminescence parameters of 6-In-11$^+$ in CD's is of interest because of the possible relation of such information to the influence of pressure on "soft" and "hard" binding sites that cause reversible structural transitions in proteins[8] and to the influence of pressure on hydrophobic interactions.

Experimental Section

Spectroscopic Measurements. Fluorescence spectra were obtained on a SPEX Fluorolog fluorimeter. Fluorescence lifetimes were measured by the single-photon counting technique. The details on the fluorescence depolarization measurements[6] and the high-pressure cell[9] were described in preceding papers. The UV absorbance spectra and ^1H NMR spectra were taken on a Cary 18 spectrophotometer and a Bruker WM-300 MHz NMR spectrometer.

Materials. 11-(3-Hexyl-1-indolyl)undecyltrimethylammonium bromide, 6-In-11$^+$, was available from previous studies.[4] α-, β-, and γ-cy-

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0002-7863/82/1504-3954$01.25/0