OURNAL OF PHYSICAL ORGANIC CHEMISTRY, VOL. 4, 125–134 (1991)

STRUCTURE AND DYNAMICS OF DICYANDIAMIDE: A THEORETICAL STUDY

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Ab initio **MO methods have been used to study the structures and energetics of dicyandiamide, $[(NH_2)_2C{=}N{-}C{\equiv}N]$, its isomers, protonated species, radical anions, transition structures for internal conformational change and transition structures for isomerization. Structures were optimized at the HF/STO-3G, HF/3–21G and HF/6–31G* levels; selected barrier heights for smaller analogues were also computed at the MP4SDTQ/6–31G* level. The most stable isomer of dicyandiamide has the cyano group on the imine nitrogen [1, $(NH_2)_2C{=}NC{\equiv}N$]; the other isomer [2, $HN{=}C(NH_2)NH{-}C{\equiv}N$] lies 12·8 kcal mol^{-1} higher. Inversion at the imino nitrogen proceeds by a linear, in plane process with a barrier of 32·5 kcal mol^{-1}. The amino rotation barriers are 19 kcal mol^{-1} (single NH_2) and 40 kcal mol^{-1} (both NH_2 in a conrotaory or a disrotatory fashion; if the NH_2 groups are allowed to pyramidalize the disrotatory barrier drops to 20 kcal mol)$^{-1}$. Protonation occurs preferentially on the imine nitrogen (PA = 219·7 kcal mol^{-1} for 1); the proton affinities PA of the amino nitrogens are 25–30 kcal mol^{-1} lower. Isomerization between 2 and 1 would go via a 1,3-sigmatropic hydrogen shift, but the barrier is high (48·3 kcal mol^{-1}); protonation reduces the hydrogen shift barrier by *ca* 15 kcal mol^{-1}. However, the most likely mechanism for isomerization involves protonation of the imine nitrogen in 2 followed by deprotonation of the cyano-substituted nitrogen to form 1, circumventing the energetically costly 1,3-sigmatropic hydrogen shift. When an electron is transferred to dicyandiamide, a sizeable fraction of the resonance stabilization of the guanidine moiety is lost.**

INTRODUCTION

Dicyandiamide (cyanoguanidine) is a highly unusual compound in that it is of both chemical and biological importance. Its engineering applications include the crosslinking of epoxide functional polymers that are useful in adhesives, composites and electronic applications. A considerable amount of experimental work has been done in an effort to define the mechanism and kinetics of the crosslinking reaction.[1] An unequivocal understanding of the mechanism of the crosslinking reaction, in addition to the nature of interfacial reactions of dicyandiamide, however, is currently lacking. Interfacial reduction reactions of dicyandiamide have been observed on zinc surfaces.[2a] These reactions have been modeled with semi-empirical MNDO calcluations.[2b] Dicyandiamide (**1**) together with its metabolites and derivatives, is also a molecule of considerable biological interest. Dicyandiamide and its monomer, cyanamide, have been observed to interact with aldehyde dehydrogenases in the liver.[3] Its derivatives have also been shown to have antihypertensive, antihistaminic and antileukemic activity. Triazine metabolites of **1** have also been found to show biological activity.[4] There is additional evidence that cyanoguanidine may have played an important role in chemical evolution.[5]

Considering the complexity of chemistry that this compound possesses, the number of theoretical studies involving dicyandiamide has been limited. Moffat[6] studied the structure of dicyandiamide and other dimerization products of cyanamide. The results of theoretical calculations have been compared with photoelectron spectroscopic and EPR results.[7] Although the structure of dicyandiamide was in question for some time,[8] it has now been firmly resolved that *N*-cyanoguanadine **1** is lower in energy than its imino form **2** (Figure 1). The main purpose of this work

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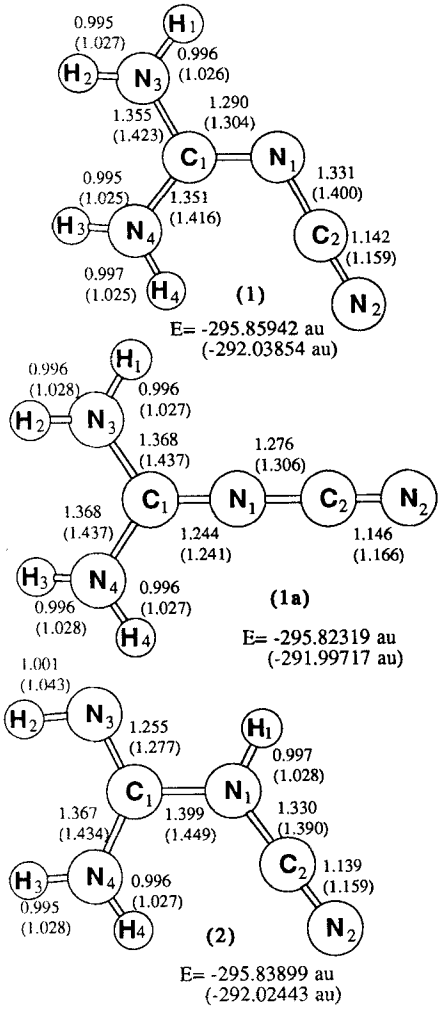
Received 3 April 1990
Revised 2 September 1990



	(1)	(1a)	(2)
<C1N1C2	117.22 (114.84)	180.0 (180.0)	125.52 (118.75)
<N1C2N2	179.53 (175.75)	180.0 (180.0)	179.47 (176.77)
<N3C1N1	118.28 (118.18)	122.99 (124.12)	116.47 (117.60)
<N4C1N1	125.77 (128.00)	122.99 (124.11)	114.46 (113.07)
<N3C1N4	115.95 (113.84)	114.03 (111.77)	129.04 (129.31)
<H1N3C1	114.64 (110.26)	115.10 (110.85)	---------
<H2N3C1	118.41 (111.74)	117.76 (111.31)	112.65 (108.66)
<H3N4C1	119.04 (112.71)	117.76 (111.22)	116.39 (111.44)
<H4N4C1	117.98 (113.28)	115.09 (110.77)	119.57 (110.98)
<H1N3H2	115.55 (110.59)	114.83 (109.94)	---------
<H3N4H4	116.09 (111.45)	114.82 (109.85)	114.65 (109.16)
<C1N1H1	---------	---------	115.12 (111.51)

Figure 1. Structures of cyanoguanidine (**1**), linear cyanoguanidine transition state (**1a**) and the isomer of cyanoguanidine (2 calculated at the HF/6–31G* level (values in parentheses are HF/STO-3G)

was to study the dynamic chemistry of dicyandiamide at a uniform level of *ab initio* theory that is sufficiently high to allow confidence in the calculated energy barriers for rotation, inversion and isomerization. We also examined the structure and thermodynamics of three protonated forms of **1** and the radical anions of both **1** and **2**. These data will provide additional information about the interfacial reactions of this highly versatile material.

METHOD OF CALCULATION

Molecular orbital calculations were carried out using the GAUSSIAN 86 program system[9a] utilizing gradient geometry optimization.[9b] Preliminary geometr optimizations utilized the STO-3G or 3–21G basis an the final geometry optimizations were carried out at th HF/6–31G* level. A full set of vibrational frequencie was calculated for all three isomerization transitio structures involving hydrogen transfer using analytic second derivatives. Only one imaginary frequency wa found for each transition structure at the 3–21G leve These first-order saddle points are therefore real trar sition states, and their structures are given in Figure 1 A frequency calculation with the STO-3G basis als established **1** and **2** to be true minima and that th transition structure **1a** for cyano inversion in **1** had single imaginary frequency. Unless noted otherwise, a

energy values given in the text were calculated with the HF/6–31G* basis set.

RESULTS AND DISCUSSION

Dicyandiamide possesses a wealth of dynamic chemistry that embodies pyramidal nitrogen inversion, steromutation at the carbon—nitrogen double bond and rotational barriers about carbon—nitrogen single bonds that are influenced by extended conjugation of two nitrogen lone pairs with the contiguous multipile bonds of the imine and nitrile moieties. We shall first address the inversion barrier about the imine nitrogen since this process probably has the least influence on the chemistry of cyanoguanidines.

In general, inversion at planar nitrogen in imines may occur by rotation about the C=N double bond, by an in-plane lateral shift process or by a combination of these two. The *Z–E* isomerization of imines is now thought to be exclusively an inversional process since torsional character about the C=N double bond in the simplest imine, methylenimine, has been rigorously excluded.[10a] In this study we assumed that a pure inversion mechanism is operating and that the transition structure at the top of the barrier height is linear in nature. The calculated inversion barrier in methylenimine (**3**) is 32·5 kcal mol^{-1} whereas Møller-Plesset electron correlation correction to full fourth order (MP4SDTQ/6–31G*//HF/6–31G*) gives a barrier of 32·6 kcal mol^{-1}. Since the Møller-Plesset correction has only a modest effect on the total energy, in the interest of uniformity we shall typically give HF/6–31G* energies in the text unless specified otherwise. The origin of this relatively high inversion barrier lies in the increase in energy of the lone pair on nitrogen as its hybridization changes from sp^2 in the ground state to pure p in the transition state attendant upon a change in the C—N—H bond angle to 180° in **3a** (Figure 2).

N-cyanoformimine (**4**) has a much reduced barrier to stereomutation (21·8 kcal mol^{-1}) since the lone pair on nitrogen can be better stabilized by resonance in the transition state **4a** than in its ground state, as shown below (the experimental barrier to topomerization in the corresponding dimethyl analogue is 18·9 kcal mol^{-1} with a coalescence temperature of 85 °C in acetone solvent). In contrast, highly electronegative substituents on nitrogen that contain lone pairs of electrons greatly increase the planar inversion barrier.[10b,c] For example, the barrier (HF/6–31G) in formaldoxime[10b] is 59·5 kcal mol^{-1} whereas the transition state for *N*-fluoroformimine (**5a**) lies 79·8 kcal mol^{-1} above its ground state **5**. In the latter case, the frontier orbital that makes the greatest contribution to the activation energy is again the lone pair on nitrogen. Surprisingly, the lone pairs on fluorine are stabilized in the transition structure. In most of these simple imines the change in energy of the C=N π bond does not make a positive contribution to the observed barrier since this orbital decreases in energy on going to the linear geometry of the transition state.

Heteroatoms (N or O) attached to the imino carbon increase the conjugation by an 'allylic-type' resonance interaction that typically results in a lowering of the imine isomerization barrier.[11,12] In order to ascertain the effect of the various substituents of dicyandiamide (**1**) on the barrier to imine isomerization, we have systematically reconstructed the molecule from its fragments. Thus, substitution of a hydrogen in methylenimine by an amino substituent affording **6** results in a decrease of 2·4 kcal mol^{-1} in the inversion barrier. The comparable exercise with *N*-cyanoformimine affording (*E*)-**7** and (*Z*)-**7** resulted in the same barrier, which would be in agreement with conventional wisdom.[11,12] Even more surprising, inclusion of the second NH_2 fragment affording cyanoguanidine (**1**) adds another 0·6 kcal mol^{-1} to the topomerization barrier (22·7 kcal mol^{-1}).

In summary, the cyano group lowers the barrier of the parent imine by 11–12 kcal mol^{-1} whereas both NH_2 substituents increase the inversion barrier in **4** by 1·7–4·2 kcal mol^{-1}. With a barrier of this magnitude, topomerization would be fairly slow at room temperature, with a half-life of the order of 1 h, and consequently inversion at imino nitrogen will not play a significant role in the solution chemistry of dicyandiamide, unless the elevated temperatures often incurred in adhesive applications are involved.

A second possible electronic perturbation of the nitrogen lone pairs on the NH_2 groups of **1** could potentially manifest itself in pyramidal nitrogen inversion. The pyramidal inversion barrier of methylamine is 6·0 kcal mol^{-1} at the HF/6–31G* level while that in NH_2CN is reduced to 1·1 kcal mol^{-1}.[13] The planar C_s conformer of **1** is only 0·6 kcal mol^{-1} higher in energy than its global minimum, suggesting that the pyramidal inversion barriers of the NH_2 substituents are sufficiently small as to be inconsequential to the dynamic chemistry of **1**. Not only is this potential energy surface shallow, but also the deviation of the NH_2 group from planarity is relatively small. The dihedral angles of the two hydrogens are only about 10–30° out of the plane of the molecule.

Although the relatively small pyramidal nitrogen barrier suggests that hybridization at nitrogen does not significantly affect the electron delocalization owing to extended conjugation, the C–N rotational barriers appear to be fairly high. Perhaps the classical example shown of a nitrogen lone pair in resonance with a

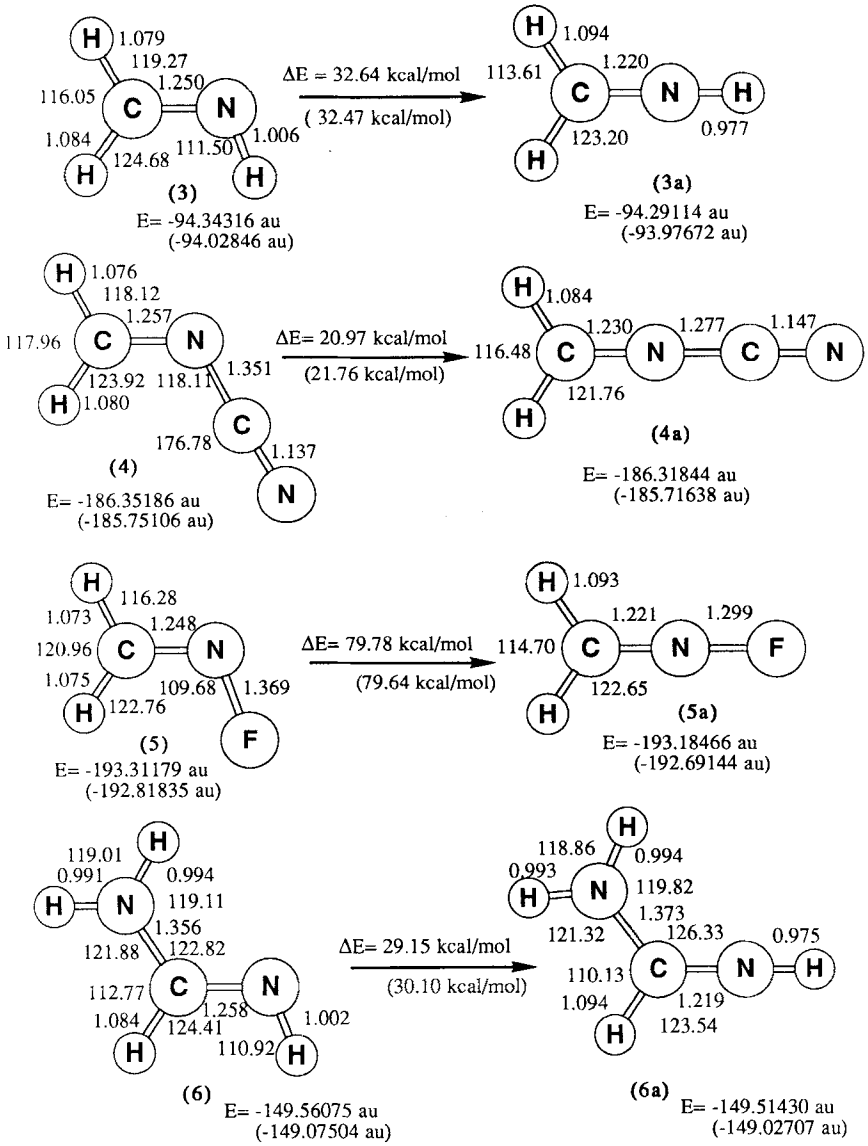


Figure 2. Comparison of structure and inversion barriers calculated at the MP4SDTQ/6–31G* level (values in parentheses ar HF/6–31G*)

multiple bond that is embodied in amide resonance is operating in **1**. The C–N rotational barriers in such compounds are typically 18–21 kcal mol^{-1}.[14a] The origin of this barrier has traditionally been ascribed to a resonance interaction, but recently alternative explanations have emerged.[14b] In its planar ground state, the nitrogen lone pair must mix with both the π and π^* orbitals of the adjacent carbonyl group.[15] The bonding combination is stabilized to a greater extent than the antibonding orbital is increased in energy, which accounts for the conformational stability of the planar structure. The same type of 'allylic' interaction is involved in **1**. We analyzed this problem by first calculating the rotational barrier for the simplest amino-substituted imine **6**. The rotational barrier of

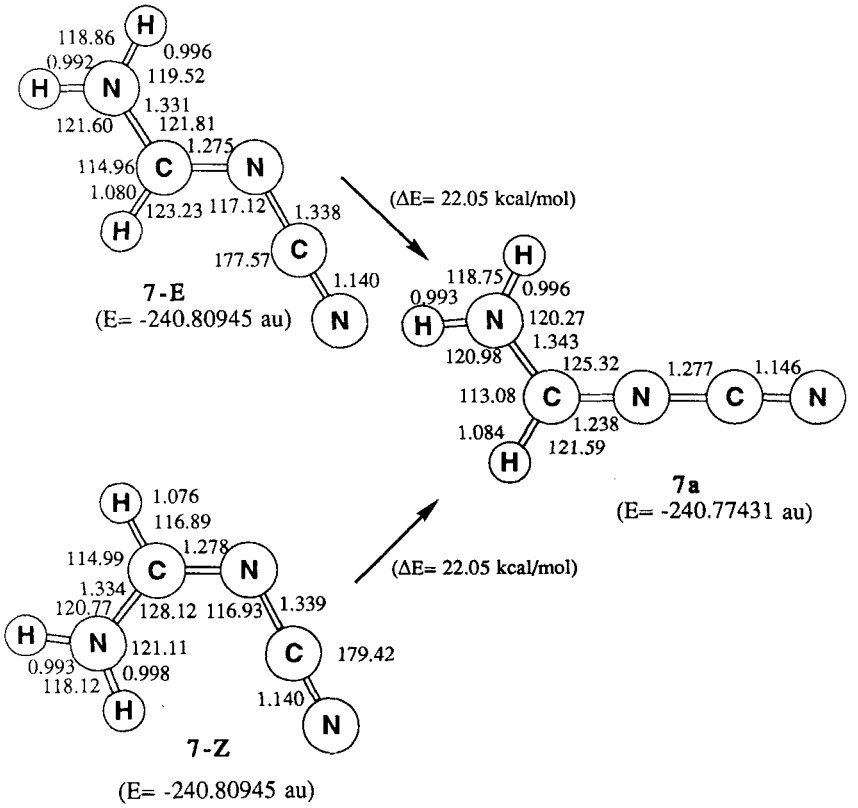


Figure 2. (*Continued*)

16·6 kcal mol^{-1} is comparable to that in an amide, and we ascribe the origin of the barrier to loss of the resonance interaction of the nitrogen lone pair when it is rotated 90° and out of conjugation with the carbon–nitrogen double bond.[14c]

The potential rotational barriers in **1** are much more complex because of the possibility of a single NH_2 group rotating out of conjugation or else the pair of them in concert in either conrotatory or disrotatory fashion. One can predict *a priori* that the single C—N bond rotational barriers should be approximately additive. The barrier for the first NH_2 group is 19 kcal mol^{-1} whereas the concerted disrotatory barrier is 40 kcal mol^{-1}, and the conrotatory pathway has a maximum 43 kcal mol^{-1} above ground-state **1**. Hence the two NH_2 groups appear to be acting independently of one another. Since the above study utilized a rigid rotation model (Table 1) for selected points along the rotational surface, we elected to optimize the geometry of one of the pertinent disrotatory 90° rotamers. The barrier was reduced to 29·0 kcal mol^{-1}, reflecting the two relatively small pyramidal nitrogen inversion barriers of the amino groups when the nitrogen lone pairs are out of conjugation.

Examination of the π molecular orbitals of ground-state **1** clearly shows the extent of electron delocalization. In the interest of simplicity the π-system of **1** can be separated into its three parts, consisting of the nitrogen (NH_2) lone pairs in extended conjugation with the two π-systems of the imine and nitrile. Molecular

Table 1. Rigid rotor rotational barriers for cyanoguanidine calculated at HF/6–31G* (STO-3G values in parentheses)

Angle	Conrotatory	Disrotatory	Single NH_2
30	5·96	10·18	4·13
	(5·92)	(5·70)	(2·82)
60	24·01	30·43	13·00
	(17·59)	(10·86)	(8·63)
90	42·91	40·27	18·87
	(26·66)	(12·48)	(12·30)
120	34·75	29·72	15·70
	(23·74)	(9·06)	(10·84)
150	13·30	10·58	7·09
	(12·58)	(5·71)	(6·14)
180	2·13	2·23	1·61
	(17·97)	(12·19)	(2·70)

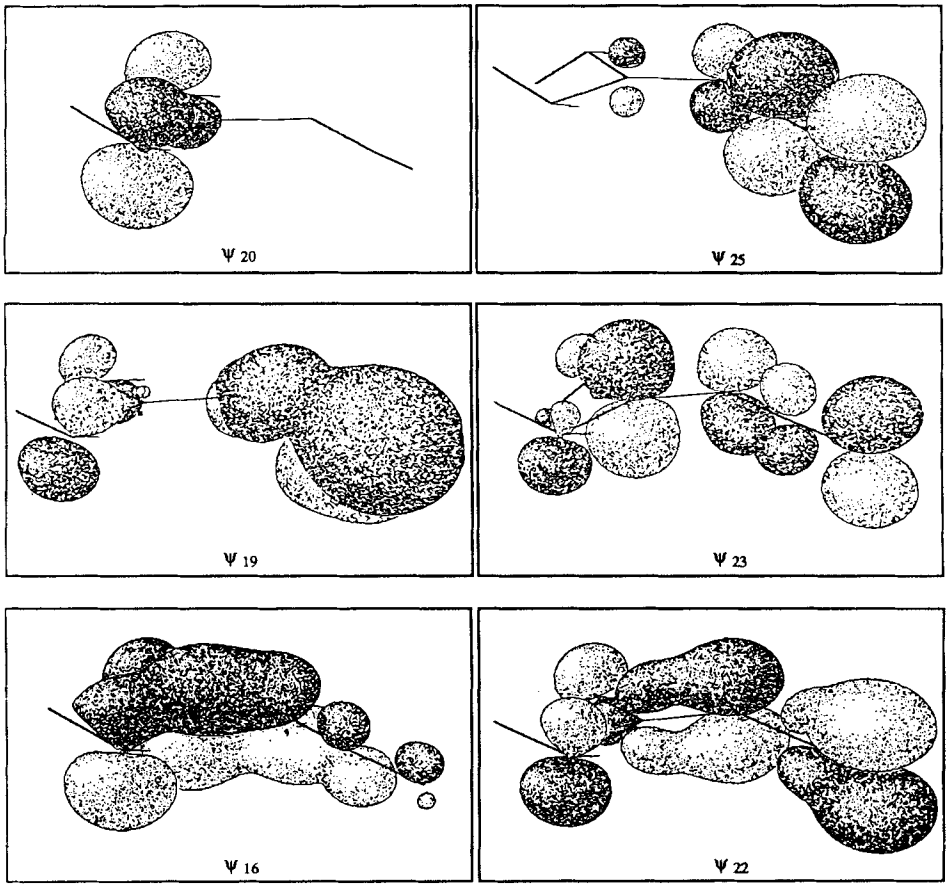


Figure 3. Molecular orbital plots of ground-state dicyandiamide (STO-3G)

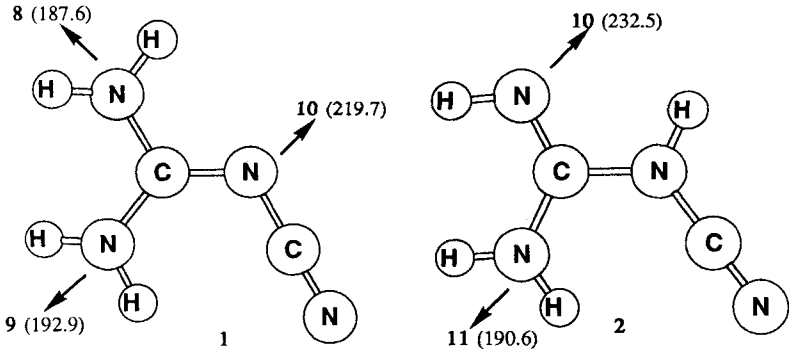
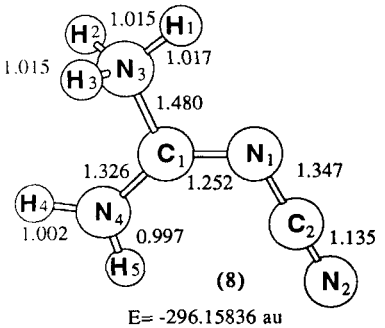


Figure 4. Proton affinities of amino and imino nitrogens in **1** and **2** (HF/6–31G*, kcal mol^{-1})

orbital plots show that the lowest lying bonding MO (ψ_{16}) has no nodes and that the eigenvectors are more heavily weighted on the NH_2 end of the molecule (Figure 3). The next highest π orbital (ψ_{19}) is localized on the C—C=N portion at the other end of molecule. The slight pyramidalization in opposite directions of the two NH_2 groups is obvious in ψ_{20}. The HOMO (ψ_{22}) is the third π orbital containing two nodes. The symmetry of this π orbital is reminiscent of ψ_2 of the 4π AO system of butadiene antibonding to the NH_2 lone pairs. The LUMO (ψ_{22}) has the same symmetry as ψ_3 of butadiene antibonding to the nitrogen lone pairs, while the highest unoccupied π MO reflects the three nodes of ψ_4 of the conjugated C=N—C=N four AO π system of **1**. These data clearly support the cross-conjugated nature of the nitrogen lone pairs with the 'dienyl' system and provide a rationalization for the relatively high 29 kcal mol^{-1} barrier attending the disrotatory rotation of the two amino substituents out of conjugation. One may conclude that barriers of this magnitude would essentially preclude either concerted con- or disrotatory rotations in favor of single-bond rotation. The lower energy pathway involving rotation about one C—N single bond at a time would obviously dominate that aspect of the dynamic chemistry of **1**.

Since it is well established that cyanamide dimeriza-



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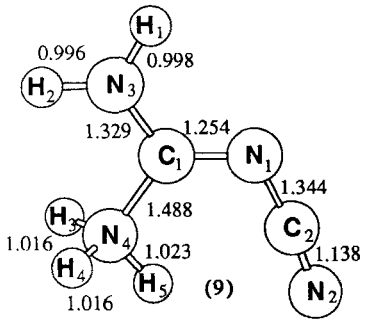

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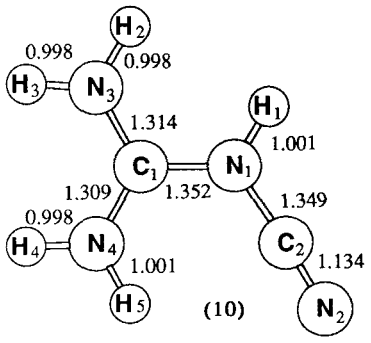
	(8)	(9)	(10)	(11)
<C1N1C2	118.29	117.72	122.18	123.41
<N1C2N2	179.63	174.66	177.59	174.43
<N3C1N1	112.25	125.41	118.34	124.13
<N4C1N1	133.15	121.01	119.73	111.11
<N3C1N4	114.60	113.58	121.93	124.76
<H1N3C1	107.05	117.10	---------	---------
<H2N3C1	112.49	123.61	122.14	120.27
<H3N3C1	112.49	---------	121.38	---------
<H3N4C1	---------	112.78	---------	110.44
<H4N4C1	124.24	112.78	121.38	112.00
<H5N4C1	118.86	109.78	121.66	112.00
<H1N3H2	108.19	119.30	---------	---------
<H2N3H3	108.28	---------	116.48	---------
<H3N4H4	---------	106.46	---------	107.82
<H4N4H5	116.90	107.34	116.96	106.55
<C1N1H1	---------	---------	120.16	116.25



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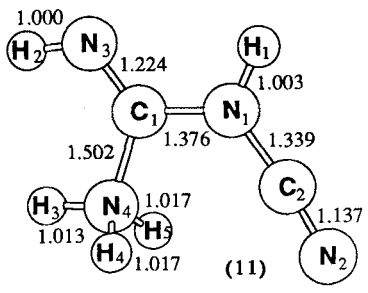
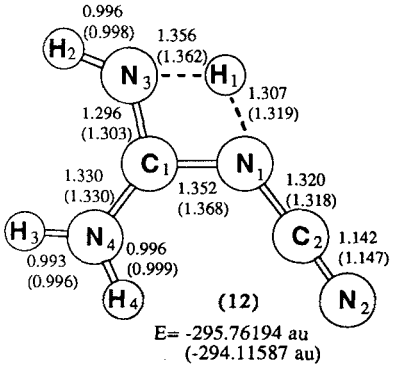
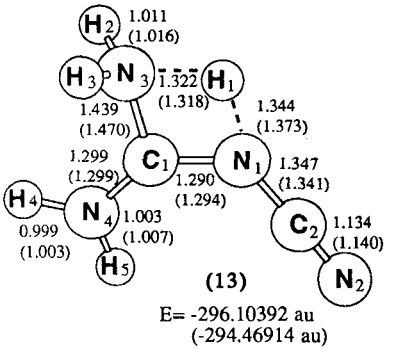


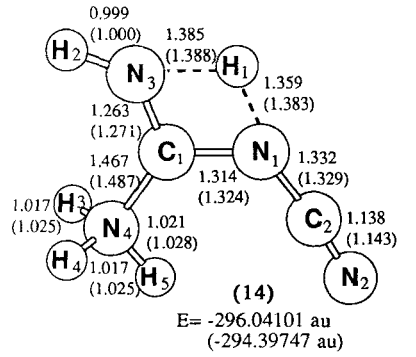
E= -296.14274 au

Figure 5. Protonated structures of cyanoguanidine calculated at the HF/6–31G* level

tion to **1** occurs under both acidic and basic conditions,[5] the relative energies of **1** and its imino isomer **2** and the barriers to their interconversion are of considerable imporance to an understanding of the multifaceted solution chemistry exhibited by dicyandiamide. We first examined the relative basicity of the more reactive nitrogens in **1**, and a summary of proton affinities is given in Figure 4. To place these reactivity parameters in proper perspective, the proton affinities of NH_3, CH_3NH_2 and CH_2NH are 217, 228 and 223 kcal mol^{-1}, respectively (experimental values for NH_3 and CH_3NH_2 are 204·0 and 214·1 kcal mol^{-1}, respectively.[16] The addition of a proton to the NH_2 groups of **1** affording the isomeric ammonium salts **8** and **9** (Figure 5) is exothermic by 187·6 and 192·9 kcal mol^{-1}, whereas the proton affinity of **2** affording the imine protonated cation **11** is 177·8 kcal mol^{-1}. The 9·8 kcal mol^{-1} difference in thermodynamic stability between cations **8** and **11** parallels the difference in energy of their respective conjugate bases, suggesting that the NH_2





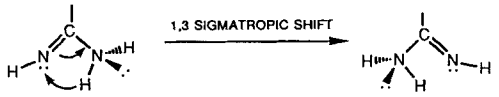


	11	12	13
<C1N1H1	77.57 (78.01)	80.061 (80.64)	75.47 (75.82)
<C1N1C2	126.26 (127.91)	125.40 (128.00)	125.28 (127.96)
<N1C2N3	179.13 (179.80)	179.20 (178.71)	174.67 (178.11)
<N3C1N1	102.69 (101.87)	100.45 (99.51)	108.80 (108.21)
<N4C1N1	125.56 (125.46)	133.52 (134.37)	122.56 (122.47)
<N3C1N4	131.75 (132.67)	126.03 (126.13)	128.64 (129.32)
<H2N3C1	124.49 (126.57)	115.44 (116.06)	129.82 (132.54)
<H3N3C1	---------	115.44 (116.06)	---------
<H3N4C1	121.21 (121.54)	---------	111.21 (111.00)
<H4N4C1	120.37 (120.52)	122.36 (122.74)	111. 21 (110.98)
<H5N4C1	---------	120.27 (120.72)	110.70 (110.32)
<H3N3H2	---------	110.17 (111.18)	---------
<H3N4H4	118.42 (117.94)	---------	107.74 (108.23)
<H4N4H5	---------	117.37 (116.54)	107.92 (108.10)

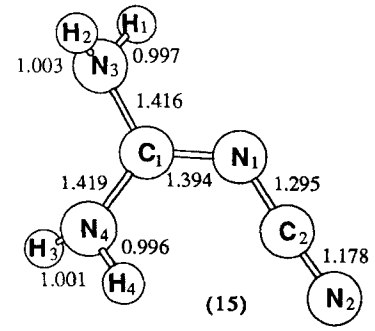
Figure 6. Transition states of cyanoguanidine and protonated cyanoguanidine calculated at the HF/6–31G* level (values in parentheses are HF/3–21G)

groups in both **1** and **2** are of comparable basicity. The imine nitrogens in both isomers of dicyandiamide are far more basic than the amino groups in **1** and **2**. The proton affinities of N-1 and N-3 in **1** and **2** are 219·7 and 232·5 kcal mol^{-1}, respectively. If the thermodynamic stability of **10** relative to isomeric cations **8**, **9** and **11** is reflected in the basicity or nucleophilicity of their conjugate bases, then the imine nitrogens in the isomeric cyanoguanidine should exhibit far greater reactivity than the amino groups. It should be noted that the difference in basicity between amino groups in CH_3NH_2 and the NH_2 groups in the larger molecules is presumably due to the electronic influence of the conjugated 'dienyl' π-system of **1**. The overall proton affinity of the larger delocalized molecule, however, is greatly increased at the imino nitrogen in the model imine, methylenimine.

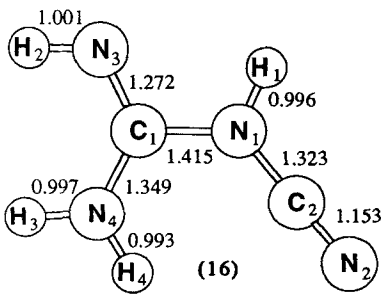
The isomerization of **1** to **2** is complicated by orbital symmetry considerations. A 1,3-sigmatropic hydrogen shift such as that involving the π bond in propene (for a theoretical discussion of allowed 1,3-sigmatropic shifts in propene, see Ref. 17) may involve a suprafacial thermally forbidden process or an antarafacial allowed process. The latter pathway has a prohibitively high barrier because of the steric considerations involving the 1,3-migration of the hydrogen from the top to the bottom face of the molecule.[17] However, an allowed process with a much more favorable geometric arrangement is also possible in 1,3-migrations involving a heteroatom at the termini with an occupied p orbital that can be placed in the nodal plane of the π-system as shown. Despite this almost idealized arrangement of atoms, the barrier for the 1,3 hydrogen migration in **1** is prohibitively high, with transition state **12** being 61·2 kcal mol^{-1} above the ground state (Figure 6). At this level of theory (HF/6–31G*), the isomeric cyanoguanidine (**2**) is 12·8 kcal mol^{-1} higher in energy than dicyanodiamide (**1**). An energy difference of 8·9 kcal mol^{-1} was calculated with the STO-3G basis set.[6] Several other cyclic dimers of much higher relative energy were also included in that study.



If one of the major pathways in the dimerization of cyanamide affording **1** involves the intermediacy of its isomer **2**, then the thermal barrier of 48·3 kcal mol^{-1} for isomerization of **2** to **1** is simply too high to make this a viable mechanistic pathway. We therefore examined two possible concerted isomerization routes involving protonated **1**. 1,3-Hydrogen migration from



E= -295.67654 au



E= -295.66535 au

	(15)	(16)
<C1N1C2	122.27	128.03
<N1C2N2	176.67	178.61
<N3C1N1	118.10	114.15
<N4C1N1	125.42	115.81
<N3C1N4	116.47	130.04
<H1N3C1	111.97	---------
<H2N3C1	115.27	115.25
<H3N4C1	116.05	118.65
<H4N4C1	115.12	123.68
<H1N3H2	112.06	---------
<H3N4H4	112.59	117.68
<C1N1H1	---------	112.62
<H1N1C2	---------	119.35

Figure 7. Structures of cyanoguanidine anion and cyanoguanidine isomer anion calculated at the UHF/6–31 + G level

an NH_3 group has a markedly reduced barrier of 34·2 kcal mol^{-1} for transition state **13**. The reaction of cation **8** going to **10** via transition state **13** is exothermic by 32·1 kcal mol^{-1}. Hydrogen transfer from cation **9**, from the neutral NH_2 group with the other one being protonated (NH_3) as shown in transition state **14**, has a barrier of 79·0 kcal mol^{-1}. The reason for the increase in activation energy of 17·7 kcal mol^{-1} relative to transition structure **12** is not immediately obvious, although the inductive effect of a positively charged ammonium group may serve to lower the electron density on the terminal nitrogen. Both barriers for rearrangement of protonated **1** appear to be high and therefore either solvent must play an important role in the rapid establishment of these equilibria, or more likely the equilibration of **1** and **2** involves protonation–deprotonation.

Finally, we shall address the structural and electronic properties of the radical anions of **1** and **2** (Figure 7). Interaction of dicyandiamide on metal surfaces obviously involves some element of electron transfer. The resulting electron density distribution of reduced **1** and **2** can afford an indication of the more probable sites of highest electron affinity. The energy differences between radical anions **15** and **16** calculated at the UHF/6–31 + G level of theory is only 7·0 kcal mol^{-1}. The LUMOs of **1** and **2** are dominated by a pπ orbital on C-1, which have, on average, an antibonding relationship with the pπ orbitals on the adjacent nitrogens (Figure 8). The distribution of electron density in the SOMOs of the radical anions is consistent with what one would predict based on the eigenvectors of the LUMO neutral **1** and **2**. As a consequence of electron transfer to the LUMO to form **15** and **16**, there is a general lengthening of the C-1-N bonds of 0·05–0·1 Å. The extra electron in the π system also decreases the stabilization that the NH_2 group can achieve by being in conjugation with the π system. Hence, there is a greater tendency for the amino groups to rotate out of the plane and to pyramidalize.

ACKNOWLEDGEMENTS

This work was supported by the Ford Motor Company. We are also grateful to the Ford Motor Company, the Pittsburgh Supercomputing Center and the Computing Center at Wayne State University for generous amounts of computing time.

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