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Molecular Orbital Calculations on Substituted Carbodiimides

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Semi-empirical SCF calculations (INDO) are used to predict barriers to internal motion in substituted carbodiimides. The barriers calculated for dimethylcarbodiimide yield no great surprises and are in excellent agreement with that observed for an alkyl substituted molecule. We also demonstrate, as found for other systems, that a substituent bearing a lone pair of electrons gives considerable nitrogen configurational stability. On the other hand, cyano substitution seems to yield a molecule that is extremely flexible with essentially no barrier to internal rotation or inversion.

Mit Hilfe von semi-empirischen SCF Berechnungen (INDO) werden die Barrieren der inneren Rotation in substituierten Carbodiimiden vorhergesagt. Die für Dimethylcarbodiimid berechneten Barrieren zeigen sehr gute Übereinstimmung mit den für die alkylsubstituierten Moleküle beobachteten Werten. Es kann ferner gezeigt werden, daß Substituenten mit einem einsamen Elektronenpaar die Stabilität der Konfiguration des Stickstoffs auch in diesem Falle erheblich erhöhen. Andererseits erhält man im Falle des Dicyanocarbodiimids ein sehr flexibles Molekül, das keine Barriere der inneren Rotation aufweist.

The configurational stability of nitrogen in structurally diverse environments has been examined by many authors using both theoretical and experimental techniques [1]. These methods demonstrate that substituents markedly change nitrogen's configurational stability. For example, substitution of a chloro group on nitrogen in aziridines dramatically increases the barrier to inversion. The invertomers of 1-chloro-2,2-dimethylaziridine have been separated and shown to be configurationally stable [2]. Similarly, N-substituted imines of benzophenone show rate constants for unimolecular *cis-trans* isomerization which vary over a range of 10^{14} [3]. It appears that substituents with lone pairs are effective in promoting nitrogen configurational stability. Computations by Dewar and Shanshal confirm these tendencies [4].

In spite of the large numbers of carbodiimides known and their synthetic importance, little is certain about their structure and the effect of substituents

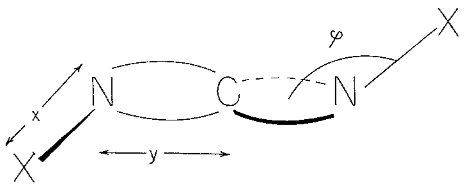

Fig. 1. Geometric parameters for disubstituted carbodiimides. x and y are N–X, C–N bond lengths, Φ the CNX angle and τ the dihedral angle between the two XNC planes

on this structure [5]. Conventional bonding theory suggests that carbodiimides have the structure given in Fig. 1, with $\Phi = 120°$ and $\tau = 90°$. If a conformation in which substituents are in orthogonal planes ($\tau = 90°$) is stable, then it is possible to envisage resolution of optical isomers. Such stability will only be found when barriers to both internal rotation and inversion about the nitrogen atoms are high. In this paper, we examine these processes using semi-empirical molecular orbital theory to estimate barrier heights.

Theory

The INDO (intermediate neglect of differential overlap) and CNDO (complete neglect of differential overlap) self-consistent-field molecular orbital methods have gained much popularity in recent years because of their applicability to a large number of systems and because of their relative simplicity compared to *ab initio* calculations. The theory and parameterization of these methods have been given elsewhere [6]. An increasing use of SCF molecular orbital theories is an attempt to reproduce and assign origins to barriers that oppose internal motion of small molecules. The INDO method of Pople and the MINDO method of Dewar [4] have been rather successful in computing such barriers in reasonably complicated systems. Gordon and Fischer [7], for example, have studied in some detail inversion and rotation barriers of a number of diazacumulenes. Dewar has successfully calculated barriers to inversion about the nitrogen atom in substituted amines [4]. The CNDO method gives inversion barriers for AB_3 molecules which are too high. Gordon and Fischer [7] point out that the INDO method gives much better agreement with experiments for these molecules. In addition, the INDO results of Gordon and Fischer compare very well with the *ab initio* calculations of Lehn and Munsch [20].

Fig. 1 gives a schematic representation of a substituted carbodiimide with labels for the important geometrical parameters that were varied. In these systems, identical conformations can be reached by either inversion or internal rotation about the nitrogen atom. For the rotational motion, we will obtain a planar transition state ($\tau = 180°$) and for the inversion, a transition state where a fragment $X-N=C$ is linear. The barriers to such motions are calculated using the INDO method in the following way. All but one geometrical parameter is kept fixed and the lowest energy is calculated, using the INDO method, as a function of the remaining parameter. Each parameter in turn is varied in this way until the minimum energy for each variable is found. The true potential minimum is then assumed to be the state which has minima for each of the geometrical variables. Such a procedure does not ensure an entirely unambiguous result for the potential minimum. We have attempted to avoid the problem of settling in a local minimum by making departures from the calculated minimum by either varying each parameter alone or in conjunction with other parameters. This procedure will then yield a calculated geometry and associated total energy for the ground state of the molecule. Barriers to internal rotation and inversion are estimated by making the appropriate change in either Φ or τ.

It is entirely possible that on inversion or internal rotation geometrical parameters other than Φ or τ change. We make the assumption that the internal

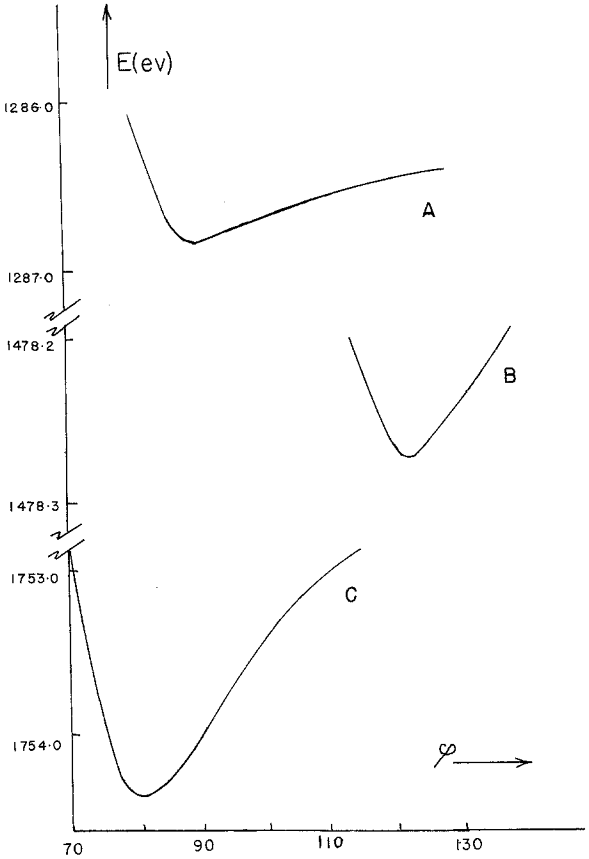

Fig. 2. Total energy as a function of the angle Φ for *A*. Dimethylcarbodiimide, *B*. Diaminocarbodiimide, and *C*. Dicyanocarbodiimide

motion is that due to the internal coordinate (Φ, τ) change alone. This common assumption implies a number of things concerning barriers to internal motion. For example, motion at one nitrogen atom will not then affect the conformation of the other nitrogens, changes in Φ and τ are treated separately. The reason for adopting such a procedure is two-fold; first, considering the internal motion of the molecule accurately one reqires a detailed knowledge of the normal coordinates of the appropriate vibrations. Such a knowledge would effectively settle the question of mixing of Φ and τ changes as well as the influence of one nitrogen atom on the other. The normal coordinates for substituted carbodiimides are not known. In addition, one of the aims of this work is to attempt to differentiate between the degree of difficulty of the inversion and internal rotation. It may well be that the barrier is controlled by a mixture of both rotation and inversion. Our calculations are aimed at seeing if one type of motion dominates the situation.

Fig. 2 shows how the total energy for the three molecules of interest vary as a function of the angle Φ. The energy shows a similar smooth variation as the other parameters x and y are changed. We note that in each of the molecules, changing the parameters gives a smooth change in the energy, that is, we can regard the energy as being approximately linearly dependant upon these geometric variables.

The observation that diferrocenylcarbodiimide had been resolved [8] as well as the initial calculations by Gordon and Fischer [7] prompted our interest in substituent effects in these molecules. The latter work emphasized the importance of substituents since their INDO calculations give a barrier to racemization of the unsubstituted compound ($H-N=C=N-H$) of about 8 kcal/mole, while that of the difluorocarbodiimide ($F-N=C=N-F$) is about 22 kcal/mole. The ground state geometries of these molecules do not differ greatly from the geometry suggested by simple bonding models. The difluoro compound has a ground state geometry in which $\Phi = 118°$ and $\tau = 93°$, while $\Phi = 115°$ and $\tau = 94°$ for unsubstituted carbodiimide. The difuoro compound is unknown and the unsubstituted carbodiimide exists only in its tautomeric form, cyanamide. Because of the tremendous practical interest in dialkylcarbodiimides [5a], we have examined the simplest member of this series, dimethylcarbodiimide [10]. In addition, we have explored the effects of more diverse substituents, diamino and dicyano. The diaminocarbodiimide, although unknown, has similarities to the known series of molecules $R_2NN=C=NR'$ [11]. In addition, the diamino molecule is simple enough to allow computational investigation. The dicyanocarbodiimide [12] was of interest because of its similarity to the tautomeric form of dicyanamide, $NC-NH-CN$, which has been postulated as an important condensing agent in prebiotic syntheses [13].

Results and Discussion

We recently reported the unusual ground state conformation of dimethylcarbodiimide [14]. The values for the geometrical parameters in various states of the molecule are given in Table 1. We assumed throughout that the CH_3 moiety is tetrahedral and the $C-H$ bond length is equal to 1.094 Å. The minimum energy of dimethylcarbodiimide corresponds to $\Phi = 90°$, $\tau = 90°$, with lengths of 1.40 and 1.26 Å for the $N-CH_3$ and $N=C$ bonds. The ninety degree value for Φ is considerably different from that found in calculations for the difluoro and unsubstituted compounds ($\simeq 120°$). Use of $\Phi = 120°$ for dimethylcarbodiimide gives an increase of about 7 kcal/mole in the total energy. Rotation of the methyl groups about the $C-N$ bond also yields a significant change in the total energy.

Table 1. *Variation of the total energy of dimethylcarbodiimide as a function of geometry. x, y, Φ and τ are illustrated in Fig. 1. The labels refer to the ground state and transition states arising from internal rotation and inversion*

	x	y	Φ	τ	E(eV)
Ground	1.40	1.26	90	90	−1286.86
	1.40	1.26	95	90	−1286.80
	1.40	1.26	85	90	−1286.75
Inverted	1.40	1.26	90	—	−1286.67
Rotated	1.40	1.26	90	180	−1286.66

Table 2. *Variation of the total energy of diaminocarbodiimide as a function of geometry*

	x	y	Φ	τ	E(eV)
Ground	1.34	1.28	123	90	−1478.27
	1.34	1.28	130	90	−1478.24
	1.34	1.28	120	90	−1478.25
Rotated	1.34	1.28	123	180	−1476.50
Inverted	1.34	1.28	123	—	−1477.46

A difference of about 1 kcal/mole is found between high and low-energy conformations, and this is probably due to the decrease in distance between hydrogen atoms of different methyl groups upon rotation. The other energies listed in Table 1 are found by assuming that on inversion, only the angle Φ is changed and on rotation about the $N=C$ bond only τ is changed. The barriers to inversion and rotation are then given by the differences between the total energies of the ground state and the state with $\Phi = 180°$ or $\tau = 180°$. Barriers calculated in this way are approximately 5 kcal/mole for the inversion process and 4.5 kcal/mole for the rotational motion. These values are in good agreement with the observations reported by Anet, Jochims and Bradley [9], who demonstrated the disymmetry of diisopropylcarbodiimide using low temperature NMR techniques and observed a free energy of activation of 6.7 kcal/mole.

Table 2 contains the geometries of the low-energy states for the appropriate conformations of diaminocarbodiimide. We first note that the calculated Φ equal to 123° approaches that calculated for the unsubstituted and the difluoro compounds closely. The amino group was assumed to have the same geometry as found for aniline, that is, an $N-H$ bond length of 1.01 Å, and $H\hat{N}H$ angle of 114° [15], and an angle of 46° between the plane containing the amino group and that containing the $N-N=C=N$ fragment of the molecule. The amino hydrogens are so disposed that the angle between the planes containing the lone pairs of the amino group and the lone pair of the carbodiimide nitrogen atom is 90°. If the substituent is assumed to remain rigid when barriers to inversion and rotation are calculated in the manner outlined earlier, then the inversion barrier is 18.5 kcal/mole^{-1} and the rotational barrier is 41.5 kcal/mole^{-1}.

The possibility of rotation about the substituent-carbodiimide bond has already been investigated for the methyl substituent. A considerable rise in the energy occurs when rotation of the amino group takes place. Thus, when electron pairs of the amino groups and carbodiimide nitrogens are *cis* or *trans* to one another in the same plane, an energy increase of 23.1 and 13.9 kcal/mole^{-1} over the 90° conformation is found. If barriers to inversion are investigated using these "ground" states in which the amino group has been rotated then transition states are found that have slightly higher energy than the transition states reported in Table 2. It may then be possible to racemize the amino compound by providing 13.9 kcal/mole^{-1} rather than the 18.5 kcal/mole^{-1} suggested by the mechanism involving only a change in the angle Φ. The main fault with this type of analysis lies in the fact that it is virtually impossible to investigate the entire surface of the potential energy for a molecule this size. The results given here indicate that

Table 3. *Variation of total energy of dicyanocarbodiimide as a function of geometry*

	x	y	Φ	τ	E(eV)
	1.37	1.28	90	90	−1753.96
[a]	1.37	1.28	90	90	−1753.56
[b]	1.37	1.28	90	90	−1753.70
	1.37	1.28	80	90	−1754.36
	1.37	1.28	80	100	−1754.43
Rotated, Ground	1.37	1.28	80	180	−1754.58
Inversion	1.37	1.28	80	—	−1753.56

[a] $N-C\equiv N=170^\circ$.

[b] $N=C=N=170^\circ$.

it is possible, however, that the order of magnitude of the barrier may be found. Calculations on propynal [16] indicate that a considerable difference in energy is found for a given out-of-plane deformation of the aldehydic hydrogen depending upon whether the internal coordinate or the normal coordinate is used. A profitable line of investigation may then involve establishing what atoms are displaced when the carbodiimide molecule vibrates in the normal mode corresponding to rotation and inversion respectively. Such an analysis limits the area of potential surface to be searched to a large extent.

The results of our calculations on dicyanocarbodiimide are unusual and intriguing. We searched through large numbers of combinations of geometric parameters and found a low energy conformation corresponding to $x=1.37$ Å, $y=1.28$ Å, $\Phi=80^\circ$, and $\tau=180^\circ$. The molecule then would seem to have a low-energy conformation which corresponds to the transition state for the rotational motion of the dimethyl and diaminocarbodiimide. Perhaps the most significant result of these calculations is that pronounced variations in parameters, especially the dihedral angle, τ, have only small effects upon the total energy. In other words, the potential well in the region covered by our parametric variations is quite flat. Even variations in the angles $N-C\equiv N$ and $N=C=N$ caused only small total energy changes. Table 3 illustrates these small variations. It seems clear that dicyanocarbodiimide is flexible, which implies that there are no significant barriers to inversion or rotation.

Our results raise a number of points. Although the method used in this paper appears capable of giving barrier information for some molecular systems, a problem lies in the assumption that a single internal coordinate is responsible for internal motion. If, in fact, the normal coordinate for internal rotation or inversion involves large changes in geometrical parameters other than Φ or τ, then the barrier estimations must await accurate normal coordinate analysis. In addition, as pointed out by Herndon, Feuer and Hall [17], semi-empirical molecular orbital methods can lead to incorrect barrier heights and geometrical conformations.

In this light our data raise interesting questions for the experimentalist. The calculated barrier heights for dimethylcarbodiimide agree well with measurements on diisopropylcarbodiimide [9]. The ground state geometry, on the other hand, with $\Phi = 90^\circ$ is rather unusual. Since the compound is known [10], a microwave structure determination would be of interest. Determination of the barriers in diaminocarbodiimide (or a substituted amino analog) represents a much more difficult problem because of the necessity of recognizing and measuring either rotation (about R_2N to N) and/or inversion (at either or both N) barriers [18]. Dicyanocarbodiimide, whose lowest energy state in our calculations varies only slightly as a function of geometrical change, has not been synthesized [12]. Its synthesis and structural determination would, of course, be important in light of our results.

The magnitude of the calculated barrier heights deserves some attention. Dimethylcarbodiimide, whose barriers to inversion and rotation are about 5 kcal/mole, is remarkably similar to unsubstituted carbodiimide with barriers of about 8 kcal/mole [7]. We feel order of magnitude of such barriers represent "normal" barriers (that is, barriers which are not highly perturbed by substituent effects). It is beyond the scope of our calculations to discuss origins of such barriers. Diaminocarbodiimide, with substantially higher barriers to both N−N rotation and inversion, poses the problem of what additional factors must be considered when substituents with lone pairs interact with nitrogen. The accepted rationale for the increase of such barriers both in rotation and inversion processes is the repulsion of lone pair electrons in the transition state [18b]. The rather nondescript ground state geometry of dicyanocarbodiimide makes discussion of barriers for this compound impossible. It should, however, be pointed out that resonance contributions of the following types should lower barriers in much the same way as has been reported for N-cyanaimines [19].

$$\mathrm{NC{-}N{=}C{=}\overset{\curvearrowright}{N}{-}C{\equiv}\underset{\curvearrowright}{N}} \leftrightarrow \mathrm{NC{-}N{=}C^{\oplus}{-}N{=}C{=}N^{\ominus}}$$

We then conclude that in spite of the assumptions inherent in calculations of the type described above, it is worthwhile to have estimates of the barriers to internal motion in substituted carbodiimides. These estimates may provide some stimulation for further experiments and act as a guide for interpreting the experimental results.

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