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## MOLECULAR STRUCTURE AND SPECTROSCOPIC PROPERTIES OF CARBODIIMIDE ( $\text{HN}=\text{C}=\text{NH}$ )

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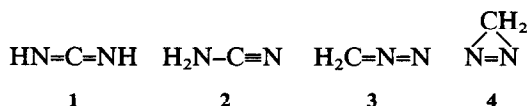
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Ab initio molecular orbital calculations, including geometry optimizations up to the level of MP3/6-31G\*\*, have been carried out for carbodiimide ( $\text{HN}=\text{C}=\text{NH}$ ). The best predicted structure for carbodiimide, which includes empirical adjustments to some geometrical parameters, has  $r(\text{N}-\text{H})=1.010$  Å,  $r(\text{C}=\text{N})=1.224$  Å,  $\angle \text{HNC}=119.7^\circ$ ,  $\angle \text{NCN}=170.8^\circ$  and  $\angle \text{HN}\dots\text{NH}=89.6^\circ$ . The calculated HNC angle shows a large variation between different levels of theory. Similar behaviour is found to occur for the related molecules, isocyanic acid ( $\text{HN}=\text{C}=\text{O}$ ) and ketenimine ( $\text{HN}=\text{C}=\text{CH}_2$ ), but not for methanimine ( $\text{HN}=\text{CH}_2$ ). The experimental observation that carbodiimide is one of the most nearly accidentally symmetric top molecules known has been confirmed. Stereomutation in carbodiimide is predicted to occur via internal rotation rather than pure inversion, but substantial ( $\approx 13^\circ$ ) opening of the HNC bond angle accompanies the torsional motion. The vibrational frequencies for carbodiimide have been calculated at the HF/6-31G\* level and empirically adjusted to yield predicted experimental values.

### 1. Introduction

Carbodiimide (**1**), a member of the (hetero)cumulene family and an isomer of well-known molecules that include cyanamide (**2**), diazomethane (**3**) and diazirine (**4**), is an intriguing molecule.



Scheme 1.

Despite the facts that  $\text{N}_2\text{N}'$ -disubstituted carbodiimides are stable compounds having a rich chemistry<sup>#1</sup> and that the parent carbodiimide (**1**) lies at the second lowest minimum on the  $\text{CH}_2\text{N}_2$  potential-energy surface [2–4], **1** has not yet been isolated, in contrast to its higher-energy isomers, **3** and **4**.

In an earlier matrix-isolation study, King and

Strope [5] observed carbodiimide (**1**) in equilibrium with its stable tautomer cyanamide (**2**) and reported that the proportion of **1** increases with increasing temperature. From the temperature dependences of the relative band intensities, they attributed four new infrared absorptions to carbodiimide (**1**). This assignment was later supported by calculations of the force field and vibrational frequencies of carbodiimide by the CNDO/2 method [6]. The frequencies predicted in this semi-empirical study for the remaining vibrational modes were, however, not corrected for systematic errors and are therefore not of much help to experimental spectroscopists.

Theoretical calculations of the rotational constants of carbodiimide have also been reported [7]. These showed that **1** has a very large  $A$  constant which is quite sensitive to the HNC bond angle. In addition, at the ab initio Hartree–Fock level of theory, this geometrical parameter turns out to be strongly basis-set dependent, which renders the theoretical prediction of the rotational spectrum of the molecule more difficult.

<sup>#1</sup> For recent reviews on the chemistry of carbodiimides see ref. [1].

Recently, the rotation–vibration spectrum of carbodiimide in the gas phase has been recorded [8–10]. Although the high-resolution spectroscopic data have allowed the determination of, *inter alia*, the rotational constants and some vibrational frequencies of carbodiimide (1), several important questions remain to be answered:

- (1) What is the molecular structure of carbodiimide (1)?
- (2) What is the mechanism of stereomutation in this molecule, rotation or inversion?
- (3) What is the form of the potential function for stereomutation?
- (4) What are the predictions for the fundamental vibrational frequencies for carbodiimide?

The present theoretical study aims to tackle these questions by means of *ab initio* molecular orbital calculations combined with empirical corrections for systematic deficiencies in the methods employed [11–13].

## 2. Method

Standard *ab initio* molecular orbital calculations were carried out with a modified version [14] of the GAUSSIAN 82 system of programs [15]. Geometries were fully optimized by use of analytical-gradient procedures at the Hartree–Fock (HF) and second-order Møller–Plesset perturbation-theory (MP2) [16] levels and by numerical-gradient methods at the third-order perturbation (MP3) level. Five basis sets were used: 6-31G\*, 6-31G\*\* [17], 6-311G\*\* [18], 6-31++G\*\* and 6-311++G\*\* [19]. Calculations at the levels of second-order (MP2), third-order (MP3), partial fourth-order (MP4 SDQ) and full fourth-order (MP4 SDTQ, abbreviated to MP4) perturbation theory, configuration interaction including all single and double excitations (CI SD), and CI SD with the Davidson correction for quadruple excitations (CI SDQ) [20], were also performed to optimize the HNC bond angle in carbodiimide and related molecules. Relative energies were obtained at the MP4/6-311G\*\* level by use of the additivity approximation:

$$\Delta E(\text{MP4/6-311G}^{**}) \approx \Delta E(\text{MP4/6-31G}^{**}) + \Delta E(\text{MP2/6-311G}^{**}) - \Delta E(\text{MP2/6-31G}^{**}). \quad (1)$$

Harmonic vibrational frequencies were calculated at the HF/6-31G\* level by use of analytical force constants.

Throughout this paper, total energies are given in hartree, relative energies in  $\text{kJ mol}^{-1}$ , bond lengths in ångström, bond angles in degree, vibrational frequencies in  $\text{cm}^{-1}$ , and rotational constants, unless otherwise noted, in GHz.

## 3. Results and discussion

### 3.1. Molecular structure of carbodiimide

Geometrical parameters and rotational constants of carbodiimide determined at seven levels of theory are given in table 1. The variation in the geometrical parameters at the Hartree–Fock level, as calculated with various basis sets, is relatively small. More significant changes are observed in going from Hartree–Fock to Møller–Plesset levels and, in particular, we note the following:

(a) For the NCN bond angle, both MP values are smaller than the HF values. The differences are somewhat larger than those noted previously for the CCN angle in ketenimine ( $\text{H}_2\text{C}=\text{C}=\text{NH}$ ) for which values of  $176.5^\circ$  and  $174.6^\circ$  were obtained by HF/6-31G\*\* and MP3/6-31G\*\* calculations, respectively [21]. Our best estimate ( $170.8^\circ$ ) of the NCN angle in carbodiimide is quite close to the values of  $166\text{--}170^\circ$  determined for X-ray crystal structures of several aliphatic and aromatic substituted carbodiimides [22].

(b) The HNC angle increases from  $118.2^\circ$  at the HF level to  $119.2^\circ$  at the MP2 level and decreases to  $116.8^\circ$  at the MP3 level. This unusual pattern (as compared with that for methanimine [23]) will be examined in detail below.

(c) The HN...NH dihedral angle decreases smoothly from HF ( $91.0^\circ$ ) to MP3 ( $89.6^\circ$ ) levels. Additional calculations at the MP4/6-31G\*\* level, employing the MP3/6-31G\*\* values for the remaining parameters, predict a value for the dihedral angle of  $90.0^\circ$ . We shall see that the nature of the rotational spectrum of carbodiimide is sensitively dependent on the value of the HN...NH dihedral angle.

Overall, the variation in calculated structure from

Table 1  
Geometrical parameters (bond lengths in Å, bond angles in degree) and rotational constant (GHz) of carbodiimide at various levels of theory

Parameter <sup>a)</sup>	HF/6-31G*	HF/6-31G**	HF/6-311G**	HF/6-31++G**	HF/6-311++G**	MP2/6-31G*	MP3/6-31G**	Pred. <sup>b)</sup>	Exp. <sup>c)</sup>
C=N	1.210	1.209	1.205	1.210	1.206	1.234	1.229	1.224	
N-H	0.999	0.999	0.999	0.999	0.999	1.015	1.010	1.010	
∠NCN	173.5	173.6	173.9	173.0	173.4	169.6	170.8	170.8	
∠HNC	118.3	118.2	117.5	118.6	118.0	119.2	116.8	119.7	
∠HN...NH (φ)	91.0	90.9	90.3	90.2	90.1	90.0	89.6	89.6	
A	373.58	373.25	367.25	376.88	371.56	371.08	356.40	379.68	379.24
B	10.625	10.640	10.719	10.620	10.705	10.211	10.338	10.365	10.367
C	10.618	10.633	10.716	10.617	10.702	10.209	10.337	10.364	10.366

<sup>a)</sup> The molecule possesses  $C_2$  symmetry.

<sup>b)</sup> Best predicted  $r_0$  structure for carbodiimide, including empirical adjustments to geometrical parameters (see text).

<sup>c)</sup> Ref. [10].

level to level affects the resulting rotational constants considerably, in particular the  $A$  constant. Paradoxically, the value obtained for the  $A$  constant at our highest level of theory (MP3/6-31G\*\*) is in poorer agreement with experiment than the values obtained at lower levels (cf. table 1); values of the  $B$  and  $C$  constants are, however, significantly improved.

In an attempt to identify the factors responsible for the discrepancies between theoretical and experimental rotational constants, the sensitivities of the rotational constants of carbodiimide with respect to changes in geometrical parameters were considered. The MP3/6-31G\*\*-optimized geometry and derived rotational constants were used as standards.

The data in table 2 show that the  $A$  constant is markedly sensitive to the value of the HNC angle and, to a smaller extent, to the N-H distance and NCN angle. It is somewhat surprising that the  $A$  constant is decreased either by widening or by narrowing of the NCN angle about its equilibrium value. The  $B$  and  $C$  constants are quite sensitive to the value of the C=N bond length. The variations in  $B$  and  $C$  with respect to the other parameters are of similar (small) magnitude and of the same sign except for those associated with changes in the dihedral angle, where the change in  $B$  constant is always positive whereas that in the  $C$  constant is always negative (table 2).

The above results suggest that the wide variation in the computed  $A$  constant is mainly due to differences in the description of the HNC angle by the various levels of theory employed. In order to obtain more information on this point, we have compared the performance of these levels of theory in describing the HNC angle in three related molecules, namely, methanimine ( $H_2C=NH$ ) as the simplest species having a C=N double bond, and ketenimine ( $H_2C=C=NH$ ) and isocyanic acid ( $HN=C=O$ ) as isoelectronic cumulene species.

For each of these four molecules, the MP3/6-31G\*\* equilibrium structure was used as reference, and its total energy, as calculated at various levels of theory, was plotted against the HNC angle. The MP3 geometries for methanimine and ketenimine were taken from refs. [24,21], respectively; additional geometry optimizations were carried out for isocyanic acid. From the results displayed in fig. 1, the following points may be noted:

(i) For methanimine, the  $\angle$  HNC values derived

Table 2

Changes in rotational constants ( $\Delta A$ ,  $\Delta B$ , and  $\Delta C$  in MHz) of carbodiimide with respect to variations in bond lengths ( $\text{\AA}$ ) and bond angles (degree)

Parameter	Variation <sup>a)</sup>	$\Delta A$	$\Delta B$	$\Delta C$
C=N	0.002/0.004 -0.002/-0.004	-57/-120 70/133	-29/-60 36/67	-29/-60 35/67
N-H	0.002/0.004 -0.002/-0.004	-1597/-2919 1071/2416	-3/-5 2/4	-3/-5 2/4
$\angle \text{NCN}$	2/3 -2/-3	-799/-1956 -1238/-2611	-9/-12 15/24	-9/-12 15/23
$\angle \text{HN...NH}$	2/4 -2/-4	-229/-440 152/322	9/12 3/8	-5/-10 -4/-9
$\angle \text{HNC}$	0.2/1.2 2.2/3.2	1688/9326 17416/25985	-4/-24 -42/-61	-4/-24 -42/-61

<sup>a)</sup> Relative to the MP3/6-31G\*\* values listed in table 1.

from correlated wavefunctions are close to one another and all compare well with the experimental value of  $110.5^\circ$ .

(ii) For the three cumulene species, the HNC angle changes appreciably from one level to another but there is a similar pattern of change: the HF value is smaller than the MP2 value (which is the largest), and the MP3 value is the smallest. Incorporation of correlation energy at the CI SD, CI SDQ or MP4 levels leads to HNC angles between the MP2 and MP3 values. The HNC angles vary monotonically along the sequence MP3, CI SD, MP4 SDQ and MP4, the changes between levels being smallest for isocyanic acid and largest for carbodiimide. The data of fig. 1 suggest a rather slow convergence of the Møller-Plesset series in the description of the HNC bond angle in these cumulene systems. In this context, the reasonably close agreement between MP2 and MP4 values may be regarded as somewhat fortuitous.

In their recent work on ketenimine [21,24], Brown and co-workers suggested, on the basis of the poor agreement between calculated and experimental rotational constants, that the MP3/6-31G\*\* value for the relevant HNC angle ( $113.7^\circ$ ) is too small. By using a fitting procedure, they obtained a value of  $115.4^\circ$  which, along with MP3 values for the remaining parameters, led to better agreement with the experimental rotational constants for this molecule. We note that their fitted value ( $115.4^\circ$ ) is  $0.4^\circ$  larger than

the value of  $115.0^\circ$  determined by the full fourth-order perturbation theory (fig. 1). In view of the slower convergence of the MP results for carbodiimide, we might expect that the true value for the HNC angle in carbodiimide should be larger than the MP4 value given in fig. 1 ( $118.5^\circ$ ) by somewhat more than  $0.4^\circ$ .

In order to obtain an improved predicted molecular structure for carbodiimide, we have used an empirical correction scheme described in detail in earlier papers [11-13]. In brief, this involves correction of the directly calculated bond lengths and bond angles ( $r_e$ ) for systematic deficiencies of the method and for vibrational averaging, by utilizing data on related species for which experimental structures ( $r_0$ ) are well established. There are no suitable reference molecules for the bond angles in carbodiimide, so only the C=N and N-H bond distances were corrected in this manner, on the basis of an analysis of structural data for methanimine, diazomethane and diazene. Results are recorded in table 3.

At each of the three levels considered, an average correction was obtained for each of the C=N and N-H bond lengths. These corrections were then used to derive predictions of corresponding bond lengths in carbodiimide. The final prediction is the average of the MP2/6-31G\* and MP3/6-31G\*\* corrected values. With these predicted values for the C=N and N-H bond lengths and the MP3/6-31G\*\*-optimized values for the NCN bond angle and HN...NH dihedral angle, best agreement with the observed rota-

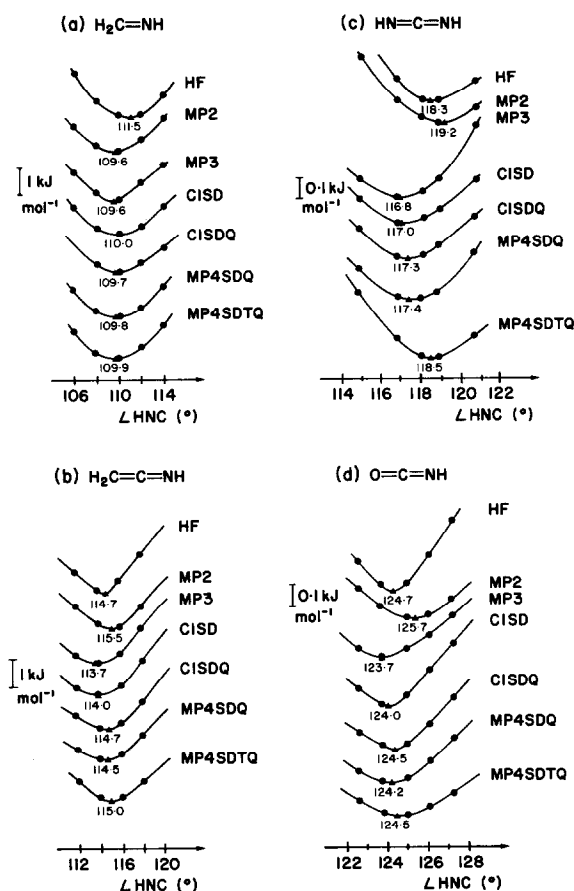


Fig. 1. Potential energy curves at different levels of theory describing HNC bond angle variation in (a) methanimine, (b) ketenimine, (c) carbodiimide, and (d) isocyanic acid 6-31G\*\* basis set.

tional constants [10] is obtained for an HNC angle of  $119.7^\circ$  (calculated values:  $A=379.57$ ,  $B=10.317$ ,  $C=10.316$  GHz). Improved agreement for the  $B$  and  $C$  constants is achieved by empirical adjustment of the  $C=N$  length. This leads to our best predicted  $r_0$  structure for carbodiimide, as shown in fig. 2, for which the calculated rotational constants are  $A=379.68$ ,  $B=10.365$  and  $C=10.364$  GHz, as compared with the experimental values [10] of 379.24, 10.367 and 10.366 GHz, respectively.

Our results confirm that carbodiimide is one of the most nearly accidentally symmetric top molecules known [10] with calculated values of Ray's asymmetry parameter  $\kappa$  ( $= (2B-A-C)/(A-C)$ ) of

$-0.999994$  (MP3/6-31G\*\* structure) or  $-0.999995$  (best predicted structure).

### 3.2. The nature of the rotational spectrum: *b*-type versus *c*-type

Because the carbodiimide molecule possesses  $C_2$  symmetry, its dipole-moment vector coincides with one of the symmetry axes (*b* or *c*) perpendicular to the principal axis, *a* [8]. Depending on whether it is the principal axis, *b* or *c*, that lies along the  $C_2$  axis, and ignoring torsional splitting, this would lead, as for HS-SH [26], to a *b*- or *c*-type pure rotational spectrum for carbodiimide.

We note initially that, for all the optimized structures listed in table 1 as well as for the predicted structure shown in fig. 2, it is the principal axis *c* that coincides with the symmetry axis. It is instructive, however, to examine the sensitivity of this conclusion to the value of the  $HN\cdots NH$  dihedral angle ( $\phi$ ).

Moments of inertia and rotational constants were calculated for a range of values of  $\phi$  in the vicinity of the equilibrium structure, using for the remaining geometric parameters the values shown in fig. 2. Examination of the results (table 4, fig. 3) shows that the *b*-rotational axis coincides with the  $C_2$  symmetry axis (implying a *b*-type spectrum) for  $\phi < 89.4^\circ$ , whereas the *c*-rotational axis coincides with the  $C_2$  symmetry axis (implying a *c*-type spectrum) for  $\phi > 89.4^\circ$ . Our best calculated value of  $\phi$  ( $89.6 \pm 1^\circ$ , fig. 2) predicts that  $|B-C| < 5$  MHz (fig. 3), as is consistent with experimental observations [10]. Again, because the predicted equilibrium value of  $\phi$  ( $89.6^\circ$ ) is so close to the crossover point from a *b*- to a *c*-type spectrum ( $89.4^\circ$ ), it is not sensible to distinguish between these possibilities on the basis of the theoretical results. Indeed, as shown previously [7] and as discussed in more detail in the following section, torsional motion in the vicinity of the equilibrium structure should occur relatively easily. Such motion would readily shift the  $C_2$  axis through the axis-switching configuration.

### 3.3. Torsion and inversion in carbodiimide

Stereomutation of carbodiimide may occur in principle via inversion or via torsion, the latter proceeding via syn or anti transition structures (fig. 4).

Table 3

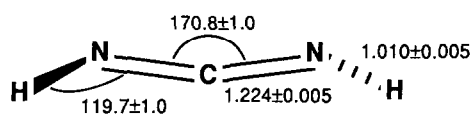
Corrections for C=N and N-H bond lengths (from structure analyses of methanimine, diazomethane and diazene) and resultant predicted bond lengths for carbodiimide

	C=N <sup>a)</sup>			N-H <sup>a)</sup>		
	HF/6-31G**	MP2/6-31G*	MP3/6-31G**	HF/6-31G**	MP2/6-31G*	MP3/6-31G**
corrections						
CH <sub>2</sub> =NH	0.023	-0.009	-0.001	0.017	-0.004	0.003
CH <sub>2</sub> =N=N	0.020	-0.007	0.000	-	-	-
HN=NH	-	-	-	0.013	-0.008	-0.001
average	0.021	-0.008	-0.001	0.015	-0.006	0.001
corrected bond lengths for carbodiimide <sup>b)</sup>						
	1.230	1.226	1.228	1.014	1.009	1.011
corrected values						
average <sup>c)</sup>		1.227			1.010	

<sup>a)</sup> Corrections are relative to experimental values: 1.273 and 1.300 for the C=N lengths in CH<sub>2</sub>=NH and CH<sub>2</sub>=N=N, respectively, and 1.023 and 1.028 for the N-H lengths in CH<sub>2</sub>=NH and HN=NH, respectively. Taken from ref. [25].

<sup>b)</sup> Relevant directly calculated values are given in table 1.

<sup>c)</sup> Taken as the average of the MP2/6-31G\* and MP3/6-31G\*\* values.



$$\angle \text{HN} \cdots \text{NH} = 89.6 \pm 1.0$$

Fig. 2. Predicted  $r_0$  structure for carbodiimide (see text).

Previous calculations [7] indicated that the torsional barrier is smaller than the inversional one, but were carried out at a modest level of theory and employed a constraint (one angle  $\angle \text{HNC} = 180^\circ$ ) in the search for an inversional transition structure.

In the present (unconstrained, higher-level) calculations, we find that the preference for inversional or torsional motion is strongly dependent on the level of theory employed. The behaviour is best illustrated by examination of a cross section of the potential en-

Table 4

Moments of inertia ( $\text{amu } \text{\AA}^2$ ) and rotational constants (GHz) of carbodiimide, calculated as a function of the HN...NH dihedral angle ( $\phi$ ) <sup>a)</sup> (degree)

$\phi$	Moment of inertia			Rotational constant		
	$I_a$	$I_b$	$I_c$	$A$	$B$	$C$
86.0	1.3296	48.720	48.800	380.05	10.371	10.355
88.6	1.3306	48.749	48.768	379.79	10.366	10.362
89.0	1.3307	48.754	48.763	379.74	10.365	10.363
89.2	1.3308	48.755	48.761	379.72	10.364	10.363
89.4	1.3309	48.758	48.758	379.70	10.364	10.364
89.6	1.3309	48.755	48.760	379.68	10.365	10.364
89.8	1.3310	48.753	48.762	379.66	10.365	10.363
90.0	1.3311	48.750	48.764	379.63	10.366	10.363
90.6	1.3313	48.743	48.770	379.57	10.367	10.361
92.0	1.3319	48.725	48.785	379.41	10.371	10.358

<sup>a)</sup> Based on the predicted structure shown in fig. 2, with the specified variations in  $\phi$ .

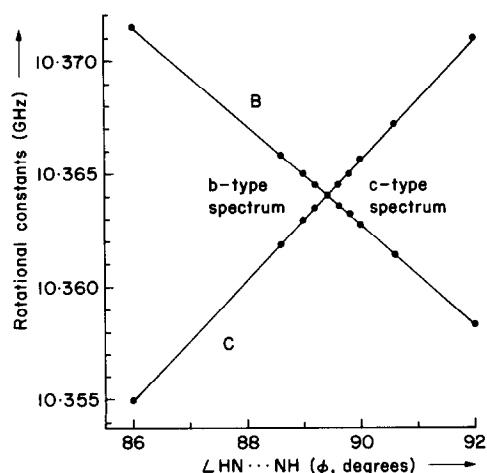


Fig. 3. Variation in calculated rotational constants of carbodiimide as a function of the HN...NH dihedral angle ( $\phi$ ) in the vicinity of the equilibrium structure.

ergy surface showing the variation in energy as a function of HNC angle ( $\beta$ ) for structures of  $C_s$  symmetry, as shown in fig. 5. In these calculations, all geometrical parameters other than  $\beta$  were optimized at each point at the appropriate level of theory.

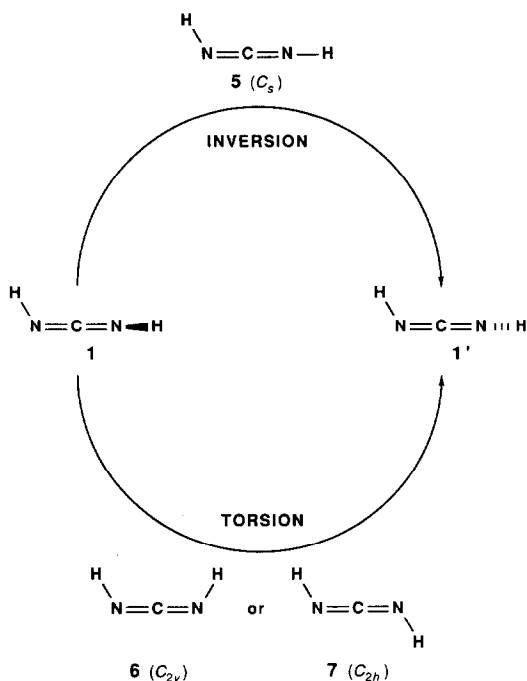


Fig. 4. Possible stereomutation processes for carbodiimide.

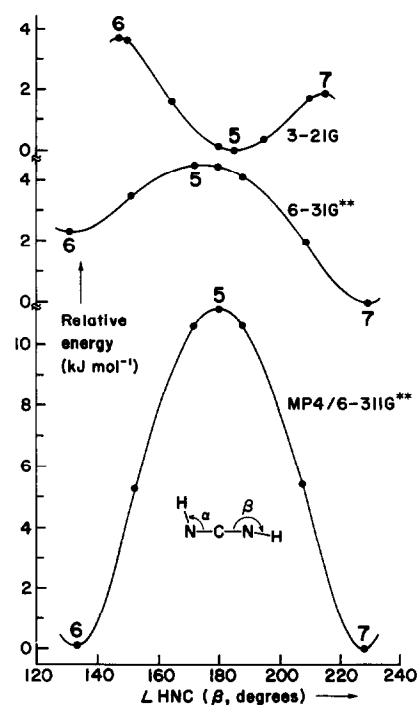


Fig. 5. Energy variation of  $C_s$ -constrained structures of carbodiimide, calculated as a function of  $\angle$  HNC.

We find that, at the HF/3-21G level, the minimum energy  $C_s$  structure (5) has  $\beta = 184.4^\circ$ , and corresponds to almost pure inversional motion; the syn ( $C_{2v}$ , 6) and anti ( $C_{2h}$ , 7) structures have higher energies. Structure 5 shows one imaginary frequency and is, therefore, a true transition structure for stereomutation in carbodiimide on the HF/3-21G surface; the syn (6) and anti (7) structures each show two imaginary frequencies at this level.

At higher levels of theory, the situation is quite different. Fig. 5 also includes results at the HF/6-31G\*\* level (with HF/6-31G\*\* optimized structures as shown in fig. 6) and at the MP4/6-311G\*\* level (utilizing HF/6-31G\*\* structures with corrections for systematic deficiencies derived from our best predicted structure in fig. 2; the corrections for  $\angle$  NCN were interpolated between zero (structure 7) and the full correction (structure 6), whereas those for  $\angle$  HNC were taken as zero for angles in the vicinity of  $180^\circ$ ,  $1.5^\circ$  (the full correction) for angles near  $130^\circ$ , and  $0.75^\circ$  for intermediate angles). At both these levels and at intermediate levels (table 5), lowest energies for  $C_s$  structures are found for the syn (6)



<sup>2</sup>) Obtained via the additivity approximation of eq. (1).

In order to obtain a more detailed description of the torsional motion, additional HF/6-31G\*\* optimizations were carried out for intermediate points with  $\angle \text{HN}\cdots\text{NH} (\phi) = 45^\circ$  and  $135^\circ$ . Single-point MP4/6-311G\*\* calculations were carried out, again using empirically corrected structures as described above. The results are presented in table 6 and in fig. 7; the latter also shows the variation in rotational constants calculated for these structures.

Our best calculations predict that the rotational barriers for syn and anti motions are virtually identical:  $33.2 \text{ kJ mol}^{-1}$  (syn, **6**) and  $33.3 \text{ kJ mol}^{-1}$  (anti, **7**).

Our calculated potential function may be fitted to a Fourier expansion

$$V(\phi) = \sum_k V_k (1 - \cos k\phi), \quad (2)$$

leading to potential constants  $V_1=0.4$ ,  $V_2=-33.2$ ,  $V_3=-0.5$  and  $V_4=1.0 \text{ kJ mol}^{-1}$ . The value of  $V(\phi)$  is heavily dominated by that of  $V_2$ , a measure of the preference of the two HNC systems to remain orthogonal [27].

The experimental millimeter-wave, submillimeter-wave and far-infrared studies of carbodiimide [10] show a small doublet splitting for all transitions up to  $K_a$  (rotational quantum number in the prolate-top limit) = 7. The largest splitting is found for  $K_a=0$  and the splitting decreases in an unusual stepwise manner. A detailed analysis, described in a separate publication [10], shows that the splitting pattern is consistent with the ab initio prediction of nearly equal syn and anti rotational barriers together with a strong

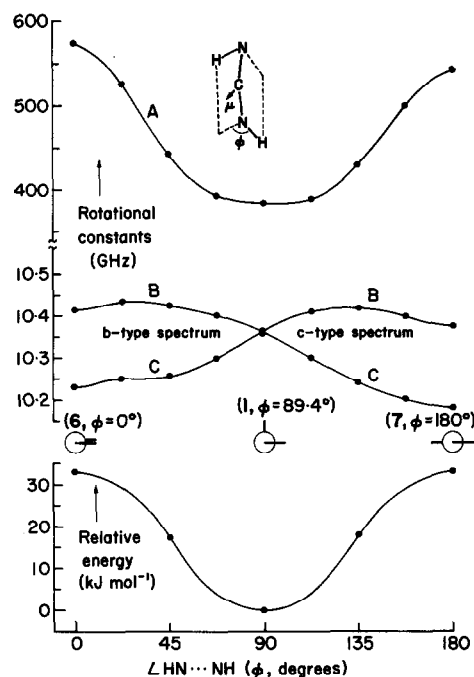


Fig. 7. Potential energy curve describing the torsional motion in carbodiimide (MP4/6-311G\*\*) together with corresponding variations in calculated rotational constants.

coupling of the HNC angle bending and torsional motions.

### 3.4. Fundamental vibrational frequencies of carbodiimide

Directly calculated vibrational frequencies at standard levels of theory (e.g., HF/6-31G\*) show signif-

Table 6

Total energies (hartree) and relative energies ( $\text{kJ mol}^{-1}$ ) (in parentheses) for points on the torsional potential energy surface of carbodiimide <sup>a)</sup>

	$\phi=0^\circ$ ( $C_{2v}$ ) ( <b>6</b> , TS)	$\phi=45^\circ$ ( $C_2$ )	$\phi=89.6^\circ$ ( $C_2$ ) ( <b>1</b> , minimum)	$\phi=135^\circ$ ( $C_2$ )	$\phi=180^\circ$ ( $C_2$ ) ( <b>7</b> , TS)
HF/6-31G**	-147.88828 (37.5)	-147.89464 (20.8)	-147.90256 (0.0)	-147.89543 (18.7)	-147.88932 (34.8)
MP2/6-31G**	-148.34651 (29.8)	-148.35184 (15.8)	-148.35786 (0.0)	-148.35159 (16.5)	-148.34649 (29.9)
MP4/6-31G**	-148.38027 (32.8)	-148.38630 (17.0)	-148.39277 (0.0)	-148.38604 (17.7)	-148.38030 (32.7)
HF/6-311G**	-147.92260 (38.0)	-147.92906 (21.1)	-147.93708 (0.0)	-147.92985 (19.0)	-147.92365 (35.3)
MP2/6-311G**	-148.40256 (30.3)	-148.40798 (16.1)	-148.41411 (0.0)	-148.40770 (16.8)	-148.40251 (30.4)
MP4/6-311G** <sup>b)</sup>	(33.3)	(17.3)	(0.0)	(18.0)	(33.2)

<sup>a)</sup> Empirically corrected geometries used (see text).

<sup>b)</sup> Obtained via the additivity approximation of eq. (1).

Table 7  
Calculated (6-31G\*) predicted and observed vibrational frequencies ( $\text{cm}^{-1}$ ) and intensities ( $\text{km mol}^{-1}$ ) of carbodiimide and carbodiimide- $d_2$

Description	Symmetry	Carbodiimide				Carbodiimide- $d_2$					
		calc. freq.	corr. factor	pred. freq.	calc. int.	obs. freq. <sup>a)</sup>	calc. freq.	corr. factor	pred. freq.	calc. int.	obs. freq. <sup>a)</sup>
NCN "in-plane" bend	a	572	0.921	527	1		488	0.945	461	2	
torsion	a	836			134		631			68	
CNH(D) sym bend	a	1022	0.895	915	17		853	0.918	782	23	
NCN sym stretch	a	1390	0.900	1250	0	(1275) <sup>b)</sup>	1366	0.924	1262	1	
NH(D) sym stretch	a	3826	0.890	3405	34		2808	0.913	2564	19	2545
NCN "out-of-plane" bend	b	572	0.921	527	112	537 <sup>c)</sup>	499	0.945	461	131	471 <sup>c)</sup>
CNH(D) asym bend	b	1014	0.895	908	551	886	855	0.918	785	230	752
NCN asym stretch	b	2354	0.898	2114	906	2097	2312	0.922	2132	883	2107
NH(D) asym stretch	b	3821	0.890	3401	155		2817	0.913	2572	251	2545

<sup>a)</sup> Taken from refs. [5,8], unless otherwise noted.

<sup>b)</sup> Calculated from combination band (CNH asym bend + NCN symmetric stretch) at  $2169 \text{ cm}^{-1}$ .

<sup>c)</sup> Reassigned on the basis of the calculated intensities.

icant systematic errors averaging about 10% [28] and are therefore of little predictive value. In an attempt to provide a set of vibrational frequencies that might be more useful in a predictive sense, we have employed a correction scheme similar to that described elsewhere [13] (for a related approach, see ref. [29] and references therein). The basis for our approach was to select a number of molecules having structural features similar to those of carbodiimide and for which experimental frequencies were available. The directly calculated frequencies for these molecules might then be used to obtain individual values of the ratio,  $\nu_{\text{exp}}/\nu_{\text{calc}}$ , for each type of vibrational mode. By judicious selection or averaging, one might hope to obtain individual factors suitable for scaling the calculated frequencies for carbodiimide.

The reference molecules selected were: methanimine, ketenimine, isocyanic acid and allene. Table 7 summarizes the selected scaling factors, and calculated (HF/6-31G\*) and predicted frequencies and intensities for both carbodiimide and carbodiimide- $d_2$  species. Available experimental values are also included for comparison purposes. We note that N-D stretching (one band only) was observed whereas N-H stretching for the parent species was not. For the three observed pairs of corresponding bands, the ratio  $\nu_{\text{exp}}/\nu_{\text{calc}}$  for the parent ( $\rho_{\text{H}}$ ) is smaller than that ( $\rho_{\text{D}}$ ) for the  $d_2$ -isotopomer, the mean value of the ratio  $\rho_{\text{H}}/\rho_{\text{D}}$  being 0.981. The corresponding ratio for ammonia/ammonia- $d_3$  is 0.982, so we feel justified in using the value 0.98 to adjust H factors to D factors (or vice-versa). For some modes, there are no suitable reference molecules; for others, there are up to four values for comparison. It is difficult to estimate precisely the errors in our predicted frequencies, but comparison between our predicted values and the observed frequencies suggests that the absolute error is less than  $30\text{--}40 \text{ cm}^{-1}$ .

#### 4. Concluding remarks

Several important points emerge from this study:

(i) Carbodiimide is predicted to be a near-symmetric-top molecule with  $|B - C| < 5 \text{ MHz}$ , in confirmation of experimental results.

(ii) The calculated HNC angle in carbodiimide and related cumulenes, ketenimine and isocyanic acid, is

found to depend sensitively on the level of theory used. The bond angle appears to be significantly underestimated even at the MP4/6-31G\*\* level.

(iii) Stereomutation in carbodiimide is predicted to occur via internal rotation rather than pure inversion, but a substantial opening of the HNC bond angle accompanies the torsional motion.

(iv) The prediction of syn and anti barriers of comparable magnitude is consistent with the experimentally observed torsional splittings.

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