

## RESEARCH NOTE

## RELATION BETWEEN FORCE CONSTANT AND BOND LENGTH FOR CARBON-NITROGEN BONDS

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**Abstract**—Using 25 accurately known bond-stretching force constants and bond lengths for 23 molecules, a relation of the form:  $F = 37.3 r^{-5.35}$  has been obtained for carbon-nitrogen bonds. The root-mean-square deviation between the force constant values reported in the literature and those calculated from the equation above is 4.09%. Fourteen of the molecules studied have a rotational symmetry axis that coincides with the carbon-to-nitrogen bond. The remaining molecules have lower symmetry. The observed force constant-bond length relationship gives quite satisfactory results for both groups of molecules.

## INTRODUCTION

LADD *et al.* [1], LADD and ORVILLE-THOMAS [2], and THOMAS *et al.* [3] have reported that an equation of the form:

$$F = a \cdot r^{-b} \quad (1)$$

or

$$\log F = \log(a) - b \cdot \log(r) \quad (2)$$

best represents the relation between the force constant  $F$  and the equilibrium bond length  $r$  for carbon-oxygen, nitrogen-oxygen, and nitrogen-nitrogen bonds, respectively. Here  $a$  and  $b$  are empirical constants which appear to have characteristic values for each specific pair of atoms. For carbon-carbon bonds and carbon-nitrogen bonds analogous relationships were first suggested some years ago [4], although at the time few molecules had been studied in sufficient detail to permit as accurate a correlation as is now possible. More recently curves have been published for both carbon-carbon and carbon-nitrogen bonds [5]. Unfortunately these two figures were not accompanied by tabulations of force constants and bond lengths employed or by calculated values for the constants  $a$  and  $b$ .

Knowledge of the values for stretching force constants of carbon-nitrogen bonds has in recent years acquired considerable importance in connection with vibrational studies of molecules related to biological systems, such as peptides [6-8], amino acids [9], nucleic acid constituents [10, 11], and proteins [12]. We have therefore reexamined the bond length-force constant relationship for carbon-nitrogen bonds by considering only molecules where both parameters can be, and have been, determined with reasonable accuracy and precision.

## SELECTION OF PERTINENT MOLECULES

To obtain a physically meaningful relationship between bond length and the corresponding bond stretching force constant, three criteria must be satisfied. (a) The molecular structure and the pertinent bond length must be accurately known. (b) It must be possible to determine a unique force constant value with reasonable accuracy. In addition, (c) the bonds studied must cover a sufficiently broad range of bond length and force constant values.

The requirements (a) and (c) are self-evident, but condition (b) merits a few extra words. As is well known, for all except the simplest and most symmetric molecules more than one set of force constants can frequently be found which will reproduce the observed frequencies equally well within the

harmonic approximation [13, 14, 15]. We have therefore tried in this study to focus largely on molecules which are either linear or that have a rotational axis of symmetry which coincides with the bond under investigation. For such molecules stretch-stretch interactions (usually involving neighboring bonds), and stretch-bend interactions with symmetric  $XH_3$  deformation modes, as in  $H_3C-NH_3^+$ , are the only interaction force constants involving the C-N bond which need to be considered. These interactions are usually well defined and relatively easily evaluated. Interactions of the C-N bond with any other vibrations have zero values because such vibrations belong to different symmetry species. In addition, we included in this study only those molecules judged to have reasonably complete force fields which were calculated, if feasible, on the basis of several isotopically substituted species.

Fourteen molecules listed in Table 1 were selected on the basis of these considerations, i.e. they have both an axis of symmetry coinciding with the C-N bond and a well-defined force field. The remaining molecules have lower symmetry but have been carefully studied. In these latter molecules the carbon-nitrogen stretching force constants are more difficult to determine because it is more difficult to select pertinent interaction force constants while performing the customary refinements [13, 14]. The results obtained on this second group of molecules do, nevertheless, agree quite well with the ones of the first category. In all cases, only molecules for which the structure is sufficiently well known from either X-ray diffraction, electron diffraction, neutron diffraction, microwave, or rotational fine-structure measurements have been included in this investigation.

## RESULTS AND DISCUSSION

Figure 1 presents a plot of  $F$  vs  $r$  (Eqn. 1). The values of the constants  $a$  and  $b$  were determined by a least squares fit of the data to Eqn. 1 using ABACUS, a Gauss-Newton iteration algorithm developed at the ERRC computer center:  $a = 37.3 \pm 0.9$ ;  $b = 5.35 \pm 0.13$ . The deviations shown are the standard errors in the estimates of the parameters. (A graph of  $\log(F)$  vs  $\log(r)$  (Eqn. 2) gives the familiar straight line plot [1-3], where the  $y$ -intercept gives  $\log(a)$  and the slope equals  $b$ .)

The force constant values calculated by Eqn. 1 with  $a$  and  $b$  set to the values above are given in Table 1 along with published literature values. It is gratifying to observe that even the force constant values predicted by this correlation for the less symmetrical molecules are not too different from the values reported in the literature. The twenty-five values

Table 1. CN bond lengths (Å) and stretching force constants (mdyn/Å)

Molecule*	Ref.	$r$	$F_{lit}$	$F_{calc}$	$\Delta F$	$\% \Delta F$
1 H <sub>3</sub> CC-NBCl <sub>3</sub>	17	1.122	18.73	20.16	-1.43	-7.11
2 H <sub>3</sub> CC-NBF <sub>3</sub>	18	1.135	18.86	18.96	-0.10	-0.51
3 C-N (B <sup>2</sup> Σ <sup>+</sup> )	19	1.150	17.169	17.67	-0.50	-2.84
4 HC-N	15	1.15321	17.88	17.41	0.47	2.71
5 H <sub>3</sub> CC-N	20	1.157	18.11	17.11	1.00	5.87
6 ClC-N	21	1.160	16.912	16.87	0.04	0.25
7 Cl <sub>3</sub> CC-N	22	1.162	17.709	16.71	0.99	5.94
8 H <sub>3</sub> CN-C	20	1.167	16.65	16.34	0.31	1.92
9 C-N <sup>+</sup> (X <sup>2</sup> Σ <sup>+</sup> )	19	1.17182	15.8820	15.98	-0.10	-0.61
10 C-N <sup>+</sup> (A <sup>1</sup> π <sub>i</sub> )	19	1.1727	15.2413	15.90	-0.66	-4.15
11 H <sub>3</sub> CN-CS	23	1.216	13.95	13.11	0.84	6.43
12 C-N <sup>+</sup> (A <sup>2</sup> Σ <sup>+</sup> )	19	1.2333	12.1626	12.15	0.01	0.08
13 H <sub>2</sub> N-CO-NH <sub>2</sub>	16	1.351	7.213	7.46	-0.25	-3.31
14 H <sub>3</sub> CCO-NHCH <sub>3</sub> ‡	8	1.386	6.415	6.50	-0.09	-1.39
15 H <sub>3</sub> C-NC	20	1.427	5.40	5.57	-0.16	-2.90
16 (-CH <sub>2</sub> CONH-) <sub>2</sub> †	6	1.449	4.922	5.13	-0.21	-4.01
17 H <sub>3</sub> C-NCS	23	1.4516	5.00	5.08	-0.08	-1.55
18 (H <sub>3</sub> C) <sub>2</sub> CH-NO	24	1.461	4.71	4.91	-0.20	-4.08
19 H <sub>3</sub> C-NH <sub>3</sub> <sup>+</sup>	25	1.465	4.82	4.84	-0.02	-0.31
20 H <sub>3</sub> C-NNN	26	1.47	4.89	4.75	0.14	3.00
21 [-(CH <sub>2</sub> ) <sub>3</sub> -NH-]§	27	1.473	4.388	4.70	-0.31	-6.56
22 H <sub>3</sub> C-NH <sub>2</sub>	28	1.474	4.97	4.68	0.29	6.24
23 <sup>+</sup> H <sub>3</sub> N-CH <sub>2</sub> COO <sup>-</sup>	9	1.48	4.34	4.58	-0.24	-5.21
24 Me <sub>3</sub> CBN-CMe <sub>3</sub>	29	1.483	4.30	4.53	-0.23	-5.06
25 F <sub>3</sub> -C-NO	30	1.555	3.626	3.51	0.11	3.19
Root-mean-square deviation:						4.09

\*Dash in the formulae indicates bond investigated, not the bond order.

†Diketopiperazine.

‡N-Methyl acetamide.

§Azetidine.

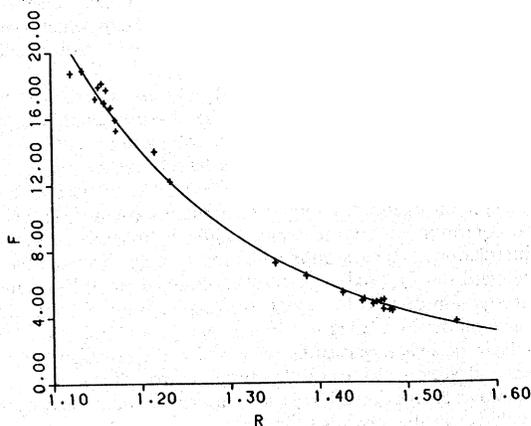


Fig. 1. Force constant,  $F$  (mdyn/Å) vs bond length,  $r$  (Å), for 25 C-N bonds of 23 molecules.

reported in Table 1 are taken from studies at seventeen different laboratories. The results imply that for biologically important model compounds, such as urea [16], *N*-methyl acetamide [8], glycine [9] and diketopiperazine [6], the values of the force constants reported in the literature are not merely convenient empirical quantities for normal coordinate calculations, but do also have real physical meaning.

In contrast to earlier work on C-O [1], N-O [2], and N-N [3], all data included in this report have been based on observed frequencies and the harmonic approximation. Thus the results calculated here cannot be better than the limitations imposed by these approximations. The possibility of

estimating the values of important stretching force constants in the manner described nevertheless offers a significant advantage for normal coordinate calculations of complex molecules. If during the customary refinements critical bond stretching force constants are fixed at these predetermined values, it becomes possible to evaluate additional interaction force constants with higher accuracy. For molecules containing carbon-oxygen bonds, such as formic acid and methyl formate [14], this advantage has been demonstrated by fixing the CO stretching force constants to values calculated by the procedure of LADD *et al.* [1]. We are currently applying an analogous approach in this laboratory to peptides and other biomolecules having carbon-to-nitrogen bonds.

Such relations may also prove useful for initial estimates of bond lengths and hence of rotational constants for diatomics and certain other small molecules in cases where the force constants can be determined directly from observed vibrational frequencies, but where analysis of the rotational fine structure is difficult.

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