NORMAL COORDINATE ANALYSIS OF DICYANODIACETYLENE

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Introduction

In earlier papers[1-3] we determined the molecular constants of various con-jugated linear systems using the "characteristic set of valence coordinates" introduced by Herranz and Castano.[4,5] The present communication deals with the normal coordinate analysis of dicyanodiacetylene—the longest known linear molecule with four conjugated triple bonds.

Results and Discussion

The vibrational assignments given by Miller and Lemmon[6] on the basis of $D_{\infty h}$ symmetry were made use of in the present calculations. Since no microwave or electron diffraction data are available the structural parameters were transferred from dicyanoacetylene. These are given in Table 1.

TABLE 1
VIBRATIONAL FREQUENCIES (cm^{-1}) AND BOND LENGTHS (Å)

$\sigma_g{}^+$	1	2235	$\sigma_u{}^+$	5	2266	π_g	8	501	π_u	11	490·5	$D = 1·19$
	2	2183		6	2097		9	455		12	276	$d = 1·14$
	3	1287·5		7	501		10	156		13	61·5	$r = 1·37$
	4	571										

The orthonormal set of symmetry coordinates,[7] transforming according to the irreducible representations of $D_{\infty h}$ point group, were constructed from the internal coordinates defined in Figure 1.

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[1] Ramaswamy, K., and Srinivasan, K., *Aust. J. Chem.*, 1968, **21**, 575.
[2] Ramaswamy, K., and Srinivasan, K., *J. molec. Structure*, 1969, **3**, 473.
[3] Ramaswamy, K., and Srinivasan, K., *Aust. J. Chem.*, 1969, **22**, 1123.
[4] Herranz, J., and Castano, F., *Spectrochim. Acta*, 1966, **22**, 1965.
[5] Herranz, J., and Castano, F., *An. R. Soc. esp. Fís. Quím. (A)*, 1966, **62**, 199.
[6] Miller, F. A., and Lemmon, D. H., *Spectrochim. Acta (A)*, 1967, **23**, 1415.
[7] Wilson, E. B. Jr., Decius, J. C., and Cross, D. C., "Molecular Vibrations." (McGraw–Hill: New York 1955.)

The symmetry coordinates for the $\sigma_g{}^+$ and $\sigma_u{}^+$ species are given below:

$\sigma_g{}^+$ species

S_1 $2^{-1/2}(\Delta d_1 + d_2)$

S_2 $2^{-1/2}(\Delta D_1 + \Delta D_2)$

S_3 $6^{-1/2}(2\Delta r_2 - \Delta r_1 - \Delta r_3)$

S_4 $3^{-1/2}(\Delta r_1 + \Delta r_2 + \Delta r_3)$

$\sigma_u{}^+$ species

S_5 $2^{-1/2}(\Delta d_1 - \Delta d_2)$

S_6 $2^{-1/2}(\Delta D_1 - \Delta D_2)$

S_7 $2^{-1/2}(\Delta r_1 - \Delta r_3)$

The F matrix elements were obtained in the usual way.[1-5] The computed valence constants are given in Table 2.
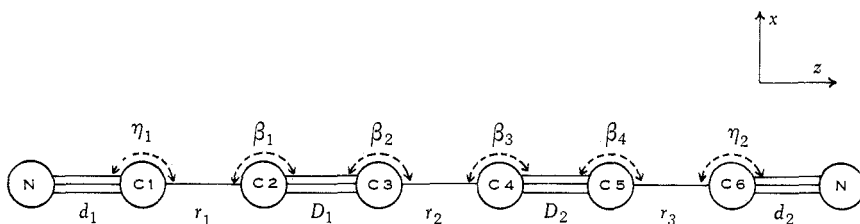

Fig. 1.—Inter-bond distances and inter-bond angles.

TABLE 2

VALENCE FORCE CONSTANTS (mdyn/Å) FOR THE TWO SETS OF CHOSEN SYMMETRY COORDINATES

f Elements	Valence Force Constants for		f Elements	Valence Force Constants for	
	Set I	Set II		Set I	Set II
$f(d)$	$40 \cdot 2984$[a]	$28 \cdot 3509$	$f(r_1 D)$	$21 \cdot 0660$	$0 \cdot 1195$
$f(r_1)$ or $f(r_3)$	$28 \cdot 8024$	$12 \cdot 8664$	$f(r_2 D)$	$25 \cdot 4226$	$4 \cdot 4231$
$f(r_2)$	$18 \cdot 4987$	$21 \cdot 6459$	$f(\beta)$	$0 \cdot 8324$	$0 \cdot 8324$
$f(D)$	$46 \cdot 2432$	$10 \cdot 4044$	$f(\eta)$	$0 \cdot 7005$	$0 \cdot 7005$
$f(dr_1)$	$26 \cdot 8087$	$6 \cdot 6492$			

[a] This number of significant figures is retained to secure internal consistency in the calculations.

TABLE 3

POTENTIAL ENERGY DISTRIBUTION FOR THE VARIOUS NORMAL MODES OF $\sigma_g{}^+$

	Set I					Set II			
	1	2	3	4		1	2	3	4
S_1	$1 \cdot 2479$	$0 \cdot 2170$	$0 \cdot 1240$	$0 \cdot 0235$	S_1	$1 \cdot 0246$	$0 \cdot 0053$	$0 \cdot 0200$	$0 \cdot 0132$
S_2	$0 \cdot 0459$	$1 \cdot 5627$	$0 \cdot 8642$	$0 \cdot 4587$	S_2	$0 \cdot 0256$	$1 \cdot 1311$	$0 \cdot 2732$	$0 \cdot 0067$
S_3	$0 \cdot 0243$	$0 \cdot 5938$	$1 \cdot 4532$	$0 \cdot 6039$	S_3	$0 \cdot 0034$	$0 \cdot 3279$	$1 \cdot 1256$	$0 \cdot 0036$
S_4	$0 \cdot 0324$	$0 \cdot 2127$	$0 \cdot 5108$	$1 \cdot 3274$	S_4	$0 \cdot 0025$	$0 \cdot 0082$	$0 \cdot 3474$	$1 \cdot 0032$

As seen from Table 2, abnormal values for the valence constants are obtained for this set. The potential energy distribution[8] for this set, given in Table 3, also

[8] Morino, Y., and Kuchitsu, K., *J. chem. Phys.*, 1952, **20**, 1809.

indicates very high mixing between the S_2, S_3, and S_4 coordinates of σ_g^+ species. Hence the following symmetry coordinates transforming according to the irreducible representation were constructed for the σ_g^+ and σ_u^+ species:

σ_g^+ species

S_1 $2^{-1/2}(\Delta d_1 + \Delta d_2)$

S_2 $20^{-1/2}(4\Delta r_2 - \Delta r_1 - \Delta r_3 - \Delta D_1 - \Delta D_2)$

S_3 $5^{-1/2}(\Delta r_1 + \Delta r_2 + \Delta r_3 + \Delta D_1 + \Delta D_2)$

S_4 $2^{-1}(\Delta r_1 + \Delta r_3 - \Delta D_1 - \Delta D_2)$

σ_u^+ species

S_5 $2^{-1/2}(\Delta d_1 - \Delta d_2)$

S_6 $2^{-1}(\Delta r_1 - \Delta r_3 - \Delta D_1 + \Delta D_2)$

S_7 $2^{-1}(\Delta r_1 - \Delta r_3 + \Delta D_1 - \Delta D_2)$

The F matrix elements were computed and the valence force constants for this set are given in Table 2. As seen from Table 2 the potential energy distribution, computed for this set, justifies our choice of symmetry coordinates.

The $f(d)$ value of $28 \cdot 35$ mdyn/Å of dicyanodiacetylene compares well with the value of $27 \cdot 62$ mdyn/Å and $26 \cdot 78$ mdyn/Å obtained in the case of dicyanoacetylene[3] and cyanoacetylene[1] respectively. In the case of the three C–C bonds, r_1, r_2, and r_3, the value obtained for the $f(r_1)$ and $f(r_3)$ is $12 \cdot 87$ mdyn/Å while the $f(r_2)$ value is $21 \cdot 65$ mdyn/Å. The value obtained for $f(D)$ is $10 \cdot 40$ mdyn/Å. While the triple bonds on either side of the central single bond appear to have weakened out, the central single bond has strengthened to such a value as to be attributed a triple bond character.