VIBRATIONAL SPECTRA AND FORCE FIELD OF AZACYCLIC COMPOUNDS.
I. PYRROLE

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For the molecules of pyrrole and its symmetric deuterated derivatives, vibrational spectra have been analyzed, and the force field has been defined in natural coordinates.

INTRODUCTION

The vibrational spectra of six-membered and five-membered azacyclic compounds were investigated fundamentally many years ago [1-3]. However, with the particular methods of calculation used in those pioneering works, the force constants of the structural elements of the rings could be determined only in the form of linear combinations of force constants of natural dependent coordinates. Therefore, in a number of recent studies [4-7], *ab initio* calculations and interpretation of the vibrational spectra of pyrrole and pyridine have been performed again, as well as empirical calculations of the force field of pyridine and its derivatives in natural coordinates. Here we must note that such calculations lead to a reexamination of the assignment of frequencies; for example, the selection of frequencies of planar vibrations of pyrrole in [7] is different from the selection that was made in [3]. Such a discrepancy makes it impossible to evaluate the available results without ambiguity, and hence further studies are required.

In the work reported here, we carried out a theoretical study of the vibrational spectra of pyrrole and its deuterated derivatives. This compound is of interest because the pyrrole ring is a structural fragment in a number of important biological compounds (tryptophan, porphyrin complexes), and its derivatives are used extensively in pharmacology. Also, it is important to define a reliable force field of pyrrole in natural coordinates, with the aim of carrying over these calculations to more complex compounds in order to interpret their vibrational spectra.

THEORETICAL

Successive solution of the direct and inverse vibrational problem involves solution of the system

$$\begin{cases} \tilde{C}KC=\Lambda \\ \tilde{C}A^{-1}C=E, \end{cases} \tag{1}$$

where A is the matrix of kinematic coefficients; K is the matrix of force constants; Λ is the diagonal matrix containing the vibrational frequencies; C is the matrix of eigenvectors; E is the unitary matrix.

The algorithm proposed in [8] for solution of the system (1) consists of the following: First, the matrix of kinematic coefficients A is diagonalized; i.e., eigenvalues λ and eigenvectors C_A are found such that

$$\tilde{C}_A A C_A=\lambda. \tag{2}$$

Then, the eigenvectors C_A are normalized

$$C'_A=C_A\lambda^{1/2} \tag{3}$$

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TABLE 1. Frequencies of Fundamental Vibrations of Pyrrole and Its Deuterated Derivatives, cm^{-1}

Assignment of vibrations	C_4NH_5		C_4NDH_4		C_4NHD_4		C_4ND_5	
	calc.	exptl.	calc.	exptl.	calc.	exptl.	calc.	exptl.
q (NH, ND)	3526	3531	2630	2607	3526	3527	2646	2609
q (CH, CD)	3176		3176		2512		2512	
q (CH, CD)	3145	3145	3148	3145	2425	2375	2410	2375
q (CH, CD)	3118	3129	3118	3131	2343	2345	2343	2342
q (CH, CD)	3117	3112	3117	3108	2336	2305	2335	2305
Q (CC, CN)	1549	1530	1545	1532	1421	1413	1438	1457
β_1 (NHC)	1474	1467	1209	1210	1479	1466	1183	
γ (CNC, CCC)	1423	1422	1413	1411	1300	1319	1300	1317
Q (CC, CN), β_1	1387	1382	1383	1388	1375	1399	1355	1327
β (HCC, DCC)	1289	1287	1289		1241		1241	
β (HCC, DCC)	1159	1144	1150		756	746	755	728
Q (CC)	1154	1134	1132	1139	1130	1164	1108	
Q (CC, NC)	1085	1074	1057	1048	1088	1092	1082	1080
β (HCC, DCC)	1024	1045	929	909	1030	953	920	908
β (HCC, DCC)	1012	1016	1012	1011	768	769	767	766
β (HCC, DCC)	717	711	716	708	522	516	522	516
β (HCC, DCC)	660	647	658		493	499	493	502
ρ (CH, CD)	874	869	866	869	833	812	832	813
ρ (CH, CD)	820	826	791	824	786	786	696	693
ρ (CH, CD)	742	734	741	732	583	598	583	570
ρ (CH, CD)	707	710	658	618	562	562	554	565
κ (CC)	600	618	600	606	466	461	462	
κ (CC)	588	601	581	603	449		443	438
ρ (NH, ND)	454	474	387	372	422		367	369

and, by means of the matrix C'_A, a new matrix of force constants K′ is constructed in accordance with the formulas

$$\tilde{C}'_A K C'_A = K'. \tag{4}$$

Determination of the eigenvalues and eigenvectors of the matrix K′ gives

$$\tilde{C}_K K' C_K = \Lambda_K^T \tag{5}$$

the theoretical frequencies Λ_K^T of which, as it is easy to show, satisfy the system (1). The eigenvectors $C = C'_A C_K$ also satisfy the system (1) and are the forms of the vibrations.

This algorithm has been used as the basis for the SCMEX program for solution of the inverse vibrational problem. If the experimental frequencies $\Lambda^{\exp}$ do not coincide with Λ_K^T, it is then possible in this last matrix to replace all or a number of the frequencies by experimental frequencies $\Lambda^{(1)}$. From Eq. (5), replacing Λ_K^T by $\Lambda^{(1)}$, we find a new matrix of force constants

$$K'^{(1)} = C_K \Lambda^{(1)} \tilde{C}_K, \tag{6}$$

which we then diagonalize in order to find the frequencies and forms of the normal vibrations.

The process is repeated until reasonable agreement is obtained between the experimental and calculated frequencies. The force field $K^{(i)}$ that gives such agreement will be the solution of the inverse vibrational problem.

An important advantage of this algorithm is that the matrices A and K can be assigned in a basis of so-called natural coordinates, which is very convenient. In the transformation (4), dependent coordinates are eliminated, since diagonalization of K′ gives (3N − 6) nonzero eigenvalues. As the final result, we obtain a matrix of vibration forms C, vibration frequencies corresponding to the experimental values, and a better-defined force field $K'^{(i)}$ that makes it possible to reproduce the experimental frequencies. This matrix $K'^{(i)}$ is obtained in independent coordinates; on the basis of Eq. (4), however, we can change over to a force field $K^{(i)}$ in natural coordinates

$$C_A \frac{1}{\sqrt{\lambda_j}} K'^{(i)} \frac{1}{\sqrt{\lambda_i}} \tilde{C}_A = K^{(i)}. \tag{7}$$

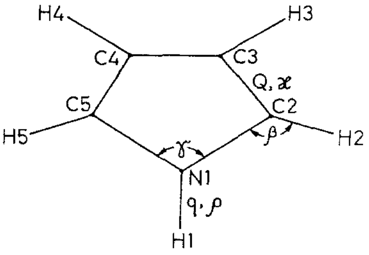

Fig. 1

Let us note that in the transformations (3) and (7), we have used all of the eigenvalues λ_i of the matrix A, however small they may be. An analogous method was proposed in [9] for solving the inverse vibrational problem by a matching method using a perturbed matrix A.

Thus, the algorithm embodied in the SCMEX program has two important features:

1) The input data are assigned in a basis of natural coordinates, and this facilitates the preparation of the data for complex molecules.

2) After solving the inverse vibrational problem, the refined force field is also obtained in natural coordinates, so that it is possible to simply carry over the force constants of the fragments and use them in subsequent calculations.

The calculations described in the following section were performed by means of a set of programs that included not only the SCMEX that we have just described, but also the KCDATA program, which facilitates the preparation of the input data, and the KINCOF program for calculation of the matrix of kinematic coefficients in natural coordinates. This set of programs was implemented for personal computers of the IBM-PC class; a system-developed menu is maintained; all programs operate in the dialogue mode, so that they can be handled successfully by personnel with very little theoretical knowledge or experience with personal computer operation.

DISCUSSION OF RESULTS

The calculation was performed in natural coordinates. The notation system used in defining the natural coordinates is shown in Fig. 1, where Q is the coordinate of stretching vibration of the C−C or C−N bond; q is the same for the C−H or N−H bond; γ describes the bending vibration of the internal angle of the ring; β describes vibration of the angle N−C−H or H−C−C; in addition, ρ is the out-of-plane vibration of the C−H bond, and κ is the out-of-plane vibration of the C−C bond. The number of dependent coordinates is 35 (5 Q-coordinates, 5 q-coordinates, 5 γ-coordinates, 10 β-coordinates, 5 ρ-coordinates, and 5 κ-coordinates.

The numerical values of the geometric parameters were taken from [10]. On the basis of these parameters, by means of the KINCOF program, we determined the matrices of kinematic coefficients for four molecules: C_4NH_5, C_4NDH_4 (replacement of H_1 atom), C_4NHD_4 (replacement of all hydrogen atoms other than H_1), and C_4ND_5.

As the zero approximation of the force field we took the force constants for pyridine and pyrrole from [1-3] for coordinates that are not coupled by additional relationships. For the coupled coordinates we performed approximate estimates as described in [3]. With such an approximation, we were able to give a preliminary interpretation of the vibrations; in particular to prefer the assignment of frequencies of planar vibrations that was made in [3] over the assignment made in [7]. Then, using the above-described SCMEX program, we carried out a refinement of the force field on the basis of experimental frequencies of four molecules. These results are presented in Table 1.

The matrix of force constants has an order of 35 and is broken up into two independent blocks (25 planar vibrations and 10 out-of-plane vibrations). In principle, each problem can be solved separately. However, the saving of time when using a modern computer is so insignificant that it is more convenient to solve the problems simultaneously, so that the change of the spectrum upon deuteration is known immediately.

As a result of the calculation, we obtained the following values for the force constants (in units of 10^6 cm^{-2}):

Diagonal force constants: $K_Q(CN) = 12{,}1$; $K_Q(C_2C_3) = 11{,}7$;
$K_Q(C_3C_4) = 10{,}0$; $K_q(NH) = 11{,}3$; $K_q(CH) = 8{,}63$; $K\gamma(CHC) = 4{,}4$; $K\gamma(NCC) =$
$= 4{,}5$; $K\gamma(CCC) = 4{,}65$; $K\beta(HNC) = 0{,}75$; $K\beta(NCH) = 0{,}60$; $K\beta(HCC) = 0{,}65$;
$K\rho(NH) = 0{,}33$; $K\rho(CH) = 0{,}51$; $K_K\ (NC) = 1{,}20$; $K_K\ (C_2C_3) = 1{,}15$;
$K_K\ (C_3C_4) = 1{,}05$;

Basic interactions: $K_{QQ}(NC, C_2C_3) = 0{,}6$; $K_{QQ}(NC, C_3C_4) = -1{,}1$;
$K_{QQ}(NC_2, NC_5) = 2{,}2$; $K_{Qq}(NC, NH_1) = 0{,}27$; $K_{Qq}(NC_2, C_2H_2) = -0{,}1$;
$K_{Q\gamma}(NC, CNC) = 1{,}55$; $K_{Q\gamma}(NC, NCC) = 1{,}65$; $K_{Q\gamma}(NC, CCC) = -0{,}5$;
$K_{Q}\beta(NC, HNC) = 0{,}1$; $K_{Q}\beta(NC, NCH) = 0{,}15$; $K_{Q}\beta(NC, HCC) = -0{,}15$;
$K_{QQ}(C_2C_3, C_3C_4) = 1{,}25$; $K_{QQ}(C_2C_3, C_4C_5) = -1{,}25$; $K_{QQ}(C_2C_3, C_5N) = -1{,}6$;
$K_{q\gamma}(C_2H_2, NC_2C_3) = 0{,}3$; $K_{q\gamma}(C_2H_2, C_2C_3C_4) = -0{,}3$.

These results do not contradict the existing data, except that the numerical values of the force constants $K_q(CH) = 9.0$ that were determined in [3], which we took as the zero approximation, gave unduly high values of the calculated vibration frequencies of the CH bonds. For our calculation, the benzene–pyridine approximation is more suitable.

As a result of our work, the inverse vibrational problem has been completely solved, and the vibrational spectra of pyrrole and its deuterated derivatives have been interpreted. In addition, these calculations have confirmed the serviceability and convenience of the proposed set of programs, which can be furnished upon written request.

In the future, we plan to continue this work, using the results we have obtained in a calculation of the indole molecule.

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