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Normal Coordinate Analysis of 1,2,4,5-Hexatetraene (Biallenyl)

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Two independent force constant calculations for 1,2,4,5-hexatetraene (biallenyl) are reported. Both results were found to be compatible with the assignment of experimental frequencies in all cases apart from the lowest B_u fundamental. This frequency has later been re-assigned on the basis of the present calculations.

Many hydrocarbons with CC double bonds in different environments have been subjected to structural and spectroscopical studies. The present work on biallenyl (1,2,4,5-hexatetraene) may be considered as a continuation of the studies of allene,[1] 1,3-butadiene,[2] butatriene,[3] and 1,3,5-hexatriene.[4] Biallenyl, C_6H_6, is a structural isomer of benzene [5] and dimethyldiacetylene.[6]

In the present work a normal coordinate analysis was performed on the basis of the recent vibrational spectra of Powell *et al.*[7] A similar analysis has also recently been performed for 1,2,4-pentatriene (vinylallene).[8] It is intended to utilize the developed force fields in computations of mean amplitudes of vibration [9] for both biallenyl and vinylallene.[10] These quantities are of great interest in electron diffraction studies. A structural investigation of biallenyl by electron diffraction has been performed,[11] and the similar work on vinylallene is in progress.[12]

NORMAL COORDINATE ANALYSIS

A molecular structure of the symmetry C_{2h} (see Fig. 1) was adopted. The structural parameters from the electron diffraction work [11] were employed.

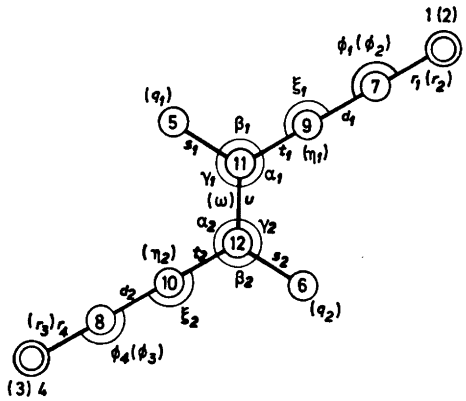

Fig. 1. The biallenyl molecular model showing the numbering of atoms and designation of the valence coordinates. Symmetrically equivalent atoms are numbered consecutively within each of the five sets. The stretchings (r) and bendings (ϕ) given in parentheses involve the atoms below the skeleton plane (Nos. 2 and 3). Otherwise the parenthesized symbols denote out-of-plane valence coordinates: linear bendings (η), out-of plane bendings (q), and torsion (ω). In addition four torsions were introduced as τ_1[1,7,11,12], τ_2[2,7,11,12], τ_3[3,8,12,11], and τ_4[4,8,12,11].

The normal modes of vibration are distributed among the symmetry species of the appropriate point group according to

$$\Gamma_{\text{vib}} = 10A_g + 5B_g + 6A_u + 9B_u$$

Force constant calculations (I). A calculation of the force field was performed in Oslo, utilizing a computer program written by Gwinn.[13] The original version of the program was modified to accept force constants for bending of three colinear atoms. The force field was based on

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valence coordinates. For the sake of simplicity the terminal hydrogens (Nos. 1, 2, 3, and 4 in Fig. 1) were excluded from the calculations, and the masses of the terminal carbon atoms adjusted accordingly.

The force constants were refined by a procedure of trial and error in order to improve the agreement with observed frequencies. In Table 1 the observed frequencies are compared with the calculated values obtained from a relatively simple force field. The corresponding force constants (stretch-stretch in mdyne/Å, bend-bend in mdyne Å/rad^2 and stretch-bend in mdyne/rad) are given in the following with reference to Fig. 1 for the designation of valence coordinates.

Stretchings: $K_s = 5.05$, $K_t = K_d = 9.5$, $K_u = 6.5$.
Bendings: $H_\alpha = 0.90$, $H_\beta = 0.45$, $H_\gamma = 0.45$.
$H_\xi = 0.37$, $H_\eta = 0.19$.
$H_q = 0.08$.
Torsion: $Y_\omega = 0.055$.
Interactions: $F_{tt} = -0.50$, $F_{td} = 0.50$, $F_{ut} = 1.5$, $F_{ud} = 1.5$, $F_{ss} = -0.35$.
$F_{\alpha\alpha} = 0.4$, $F_{\gamma\gamma} = 0.2$.
$F_{\xi\xi} = 0.10$, $F_{\eta\eta} = 0.15$.
$F_{qq} = 0.03$.
$F_{u\gamma} = 0.7$.

Force constant calculations (II). Independently of the calculations (I) a more elaborate analysis of the force constants was performed in Trondheim. All the hydrogen atoms were included in the twelve-atomic model of the molecule. The secular equation of the vibrational problem was solved in terms of symmetry coordinates, in contrast to the approach of the calculations (I). The well-known GF matrix method of Wilson [14] was applied, utilizing well-established computer programs.

An initial approximate force field was estimated by means of force constants transferred from allene,[1] in part from butatriene,[3] and from hexatriene.[4] Additional force constants were guessed in the first run. Some details of these calculations are reported elsewhere.[8] The calculated frequencies are included in Table 1. The force field was tentatively adjusted to fit the observed frequencies from Powell *et al.*[7] through trials and errors and through several steps of iteration. During these refinements several seemingly meaningful interaction force constants were introduced, and the values of principal force constants were modified. It was found possible to reproduce all of the assigned fundamentals from Powell *et al.*[7] with seemingly reasonable force constants except for one frequency. In the experimental work [7] the 333 cm^{-1} band is assigned as the lowest B_u frequency (ν_{30}). The present calculations suggest rather a value around 130 cm^{-1} or at least below 170 cm^{-1}. In the following we give the list of valence force constants from the final force field. This force field is compatible with the assignment of Powell *et al.*[7] except for $\nu_{30} = 130$ cm^{-1}. All values are in mdyne/Å. The symbols are supposed to be self-explanatory when reference is made to the notation defined in Fig. 1.

Table 1. Observed fundamental frequencies (cm^{-1}) and those from the calculations.

Species	Observed [7,8]	Calculated (I)	(II)
A_g	3005	3010	3019
	2985	–	2994
	1934	1976	1948
	1455	–	1501
	1383	1369	1405
	1352	1316	1257
	1142	1062	1103
	1012	–	867
	525	535	509
	228	282	251
A_u	3070	–	3062
	885	–	964
	793	–	736
	674	690	688
	283	309	268
	90	84	81
B_g	3057	–	3063
	1087	–	1108
	860	–	842
	652	651	684
	311	316	298
B_u	3100	3095	3022
	3000	–	2993
	1957	1990	1933
	1432	–	1462
	1241	1058	1321
	1216	1231	1176
	854	–	825
	522	507	551
	333[a] / 110[b]	130	133

[a] From Ref. 7. [b] Re-assigned in Ref. 8.

Stretchings: $f_{rr}^{(1)}(r_1r_1) = 4.99$, $f_{rr}^{(2)}(r_1r_2) = 0.01$, $f_{rr}^{(3)}(r_1r_3) = -0.03$, $f_{rr}^{(4)}(r_1r_4) = 0.00$.
$f_{ss}^{(1)} = 5.10$, $f_{ss}^{(2)} = -0.15$.
$f_{dd}^{(1)} = 10.83$, $f_{dd}^{(2)} = -0.31$.
$f_{tt}^{(1)} = 10.79$, $f_{tt}^{(2)} = -0.20$.
$f_u = 7.34$.
Bendings (including linear and out-of-plane): $f_{\phi\phi}^{(1)} = 0.64$, $f_{\phi\phi}^{(2)} = 0.30$, $f_{\phi\phi}^{(3)} = 0.03$, $f_{\phi\phi}^{(4)} = -0.02$.
$f_{\beta\beta}^{(1)} = 0.68$, $f_{\beta\beta}^{(2)} = 0.01$.
$f_{\gamma\gamma}^{(1)} = 0.70$, $f_{\gamma\gamma}^{(2)} = 0.04$.
$f_{\xi\xi}^{(1)} = 0.24$, $f_{\xi\xi}^{(2)} = 0.01$.
$f_{\eta\eta}^{(1)} = 0.16$, $f_{\eta\eta}^{(2)} = 0.03$.
$f_{qq}^{(1)} = 0.15$, $f_{qq}^{(2)} = -0.01$.
Torsions: $f_{\tau\tau}^{(1)} = 0.20$, $f_{\tau\tau}^{(2)} = -0.03$, $f_{\tau\tau}^{(3)} = 0.00$, $f_{\tau\tau}^{(4)} = 0.04$.
$f_\omega = 0.0637$.
Interactions for coordinates of different types:
$f_{rd}^{(1)} = 0.18$, $f_{rd}^{(2)} = 0.00$.
$f_{r\phi}^{(1)} = 0.18$, $f_{r\phi}^{(2)} = 0.12$, $f_{r\phi}^{(3)} = -0.02$, $f_{r\phi}^{(4)} = 0.02$.
$f_{s\beta}^{(1)} = 0.15$, $f_{s\beta}^{(2)} = 0.02$.
$f_{s\gamma}^{(1)} = 0.15$, $f_{s\gamma}^{(2)} = 0.05$.
$f_{du} = 0.46$, $f_{tu} = 1.45$.
$f_{d\phi}^{(1)} = 0.33$, $f_{d\phi}^{(2)} = 0.00$.
$f_{t\beta}^{(1)} = 0.29$, $f_{t\beta}^{(2)} = -0.07$.
$f_{t\gamma}^{(1)} = -0.20$, $f_{t\gamma}^{(2)} = 0.16$.
$f_{u\beta} = -0.15$, $f_{u\gamma} = 0.31$.
$f_{\beta\gamma}^{(1)} = 0.33$, $f_{\beta\gamma}^{(2)} = 0.00$.

CONCLUSION

Results obtained from an analysis using Gwinn's program and from programs using Wilson's GF method should of course not differ in the physical sense.

From the both independent calculations (I) and (II) it was concluded that the force constant analysis confirms the assignment of experimental frequencies of Powell *et al.*[7] except for the lowest B_u fundamental, ν_{30} (333 cm^{-1}). It was found impossible to modify the force fields so as to be compatible with $\nu_{30} = 333$ cm^{-1} without introducing unreasonable force constant values. The ν_{30} fundamental was re-assigned [8] on the basis of the present calculations. Three candidates for this fundamental were detected as weak infrared bands at 150, 130, and 110 cm^{-1} with a slight preferance for 110 cm^{-1}. In that case it is easiest to explain 333 cm^{-1} as a combination band. Anyone of the three values proposed as the re-assigned ν_{30} fundamental are compatible with reasonable force constant values.

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