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Mean Amplitudes of Vibration for Biphenylene

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With 2 Figures

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A normal coordinate analysis for the in-plane vibrations of biphenylene was performed. Calculated values of mean amplitudes of vibration for all interatomic distance types in biphenylene and biphenylene-d_8 are given.

Many structural and spectral investigations have been performed for aromatic hydrocarbons. *Almenningen* et al.[1] have reported an electron diffraction structure investigation of naphthalene, anthracene and coronene. Mean amplitudes of vibration[2] have been determined by electron diffraction for benzene[3, 4] biphenyl[5] and azulene[6]. Calculated values of mean amplitudes from spectroscopic data have been deduced for benzene[7–9], naphthalene[9–11], anthracene[11] and azulene[12].

An excellent paper on the in-plane vibrational spectrum of biphenylene ($C_{12}H_8$) and some of its isotopic molecules has appeared recently[13]. A calculation of the mean amplitudes from these data seems to be a useful supplement to the previous work mentioned above.

The present calculations were based on symmetry coordinate expressions taken from a similar analysis of the naphthalene model[14] with necessary adaptations. Only the in-plane vibrations were treated. Fig. 1 shows the stretching and bending valence coordinates used in addition to those from the naphthalene model. Below we specify the new symmetry coordinates.

In species A_g the third coordinate was substituted by

$$S_3(A_g) = 2^{-1/2}\,(u_1 + u_2)$$

and a new coordinate was added

$$S_{10}(A_g) = 2^{-1/2}\,(w_1 + w_2).$$

In species B_{3g} the following coordinate was added:

$$S_9(B_{3g}) = \tfrac{1}{2}\,(UW)^{1/2}(\rho_1 - \rho_2 + \rho_3 - \rho_4).$$

The symbols U and W denote the appropriate equilibrium C—C distances (cf. Fig. 1).

Species B_{1u}:

$$S_9(B_{1u}) = 2^{-1/2}\,(w_1 - w_2).$$

Species B_{2u}:

$$S_9(B_{2u}) = 2^{-1/2}\,(u_1 - u_2).$$

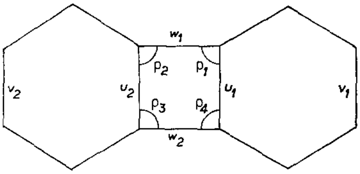

Fig. 1. Valence coordinates used in addition to those from the naphthalene model; cf. Ref. [14]

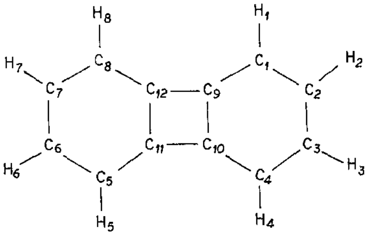

Fig. 2. Identification of the atoms in biphenylene

As an aid in developing the force constants we have furthermore applied the following redundant coordinates.

$$\begin{aligned}
S_{11}^*(A_g) &= 2^{-1/2}\,(v_1 + v_2),\\
S_{10}^*(B_{1u}) &= \tfrac{1}{2}\,(UW)^{1/2}(\rho_1 + \rho_2 - \rho_3 - \rho_4),\\
S_{10}^*(B_{2u}) &= 2^{-1/2}\,(v_1 - v_2),\\
S_{11}^*(B_{2u}) &= \tfrac{1}{2}\,(UW)^{1/2}(\rho_1 - \rho_2 - \rho_3 + \rho_4).
\end{aligned}$$

The species A_g also contains the redundant zero coordinate:

$$S_{12}^*(A_g) = \tfrac{1}{2}\,(UW)^{1/2}(\rho_1 + \rho_2 + \rho_3 + \rho_4).$$

It should be noted that the species designations used above do not conform with *Mulliken*'s conventions[15]. That is because we have adopted the notation from naphthalene. According to *Mulliken* our B_{1u} and B_{2u} symbols should be interchanged.

Table 1. *Mean Amplitudes of Vibration (in Å Units) for Biphenylene and Biphenylene*-d_8

Distance*	Equil. dist.	$C_{12}H_8$		$C_{12}D_8$	
		0 K	298 K	0 K	298 K
Bonded distances					
C-2—C-1	1.423	0.046	0.046	0.046	0.046
C-2—C-3	1.385	0.046	0.046	0.046	0.046
C-1—C-9	1.372	0.045	0.046	0.045	0.046
C-9—C-12	1.514	0.044	0.044	0.044	0.044
C-9—C-10	1.426	0.044	0.044	0.044	0.044
C-2—H-2	1.060	0.077	0.077	0.066	0.066
C-1—H-1	1.060	0.077	0.077	0.066	0.066
Nonbonded C ··· C distances					
C-2—C-9	2.366	0.053	0.056	0.053	0.055
C-2—C-10	2.752	0.057	0.062	0.057	0.062
C-2—C-4	2.456	0.052	0.053	0.052	0.053
C-1—C-4	2.893	0.057	0.058	0.056	0.058
C-1—C-10	2.451	0.054	0.057	0.054	0.057
C-9—C-11	2.080	0.044	0.045	0.044	0.045
C-2—C-12	3.880	0.056	0.059	0.055	0.059
C-2—C-11	4.127	0.055	0.058	0.055	0.058
C-1—C-12	2.772	0.054	0.057	0.054	0.057
C-1—C-11	3.437	0.051	0.052	0.051	0.052
C-2—C-8	5.096	0.063	0.074	0.063	0.074
C-2—C-7	6.246	0.062	0.069	0.061	0.069
C-2—C-6	6.398	0.061	0.067	0.061	0.066
C-2—C-5	5.475	0.061	0.067	0.060	0.067
C-1—C-8	3.833	0.064	0.077	0.064	0.077
C-1—C-5	4.802	0.057	0.059	0.057	0.059
Nonbonded C ··· H distances					
C-2—H-3	2.113	0.104	0.105	0.090	0.092
C-2—H-1	2.181	0.105	0.106	0.090	0.093
C-2—H-4	3.420	0.098	0.099	0.086	0.088
C-1—H-2	2.147	0.103	0.103	0.089	0.090
C-1—H-3	3.405	0.097	0.098	0.085	0.087
C-1—H-4	3.953	0.092	0.093	0.081	0.083
C-9—H-1	2.134	0.101	0.102	0.087	0.089
C-9—H-2	3.330	0.095	0.096	0.082	0.084
C-9—H-3	3.812	0.093	0.095	0.082	0.085
C-9—H-4	3.421	0.095	0.096	0.083	0.085
C-2—H-8	5.353	0.142	0.157	0.123	0.143
C-2—H-7	7.192	0.104	0.109	0.091	0.099
C-2—H-6	7.421	0.097	0.101	0.086	0.091
C-2—H-5	5.967	0.131	0.141	0.114	0.128
C-1—H-8	3.974	0.144	0.160	0.126	0.147
C-1—H-7	5.972	0.109	0.117	0.096	0.106
C-1—H-6	6.530	0.095	0.099	0.084	0.089

Table 1 (continued)

Distance*	Equil. dist.	$C_{12}H_8$ 0 K	$C_{12}H_8$ 298 K	$C_{12}D_8$ 0 K	$C_{12}D_8$ 298 K
C-1—H-5	5.504	0.117	0.121	0.102	0.108
C-9—H-8	3.217	0.127	0.131	0.109	0.117
C-9—H-7	4.833	0.098	0.100	0.086	0.089
C-9—H-6	5.176	0.091	0.093	0.080	0.083
C-9—H-5	4.183	0.110	0.112	0.095	0.099
H ··· H distances					
H-2—H-1	2.501	0.168	0.170	0.142	0.147
H-2—H-3	2.413	0.167	0.169	0.141	0.145
H-2—H-4	4.284	0.138	0.139	0.117	0.120
H-1—H-4	5.013	0.117	0.117	0.100	0.101
H-2—H-8	6.104	0.176	0.191	0.150	0.172
H-2—H-7	8.101	0.137	0.143	0.117	0.126
H-2—H-6	8.452	0.122	0.125	0.105	0.108
H-2—H-5	7.025	0.151	0.160	0.129	0.141
H-1—H-8	3.826	0.200	0.223	0.172	0.203
H-1—H-5	6.307	0.146	0.149	0.124	0.129

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* In this column H designates ^1H or $^2H = D$ for $C_{12}H_8$ and $C_{12}D_8$, respectively.

The mean amplitudes of vibration were computed from a harmonic force field which was adjusted to fit exactly the observed frequencies[13] for $C_{12}H_8$. The structural parameters were taken from a crystal work[16]. For the sake of brevity we do not report any details of this force constant analysis. A complete listing of the force constants based on the symmetry coordinates is available on request to the authors.

Table 1 shows the calculated mean amplitudes of vibration for all types of distances in $C_{12}H_8$ and $C_{12}D_8$ at two temperatures, viz. absolute zero and 298 K. The identification of the atoms is shown in Fig. 2. Table 1 gives also the equilibrium distances (in Å units) calculated from the adopted structural parameters. All the mean amplitudes are found to have reasonable magnitudes on comparing them with the corresponding ones in related molecules, especially naphthalene[9, 11]. The new types of bonded C—C distances, viz. C-9—C-10 and C-9—C-12, tend to have slightly smaller mean amplitudes than the rest of the CC bonds. This difference ($\approx$ 0.002 Å) is not necessarily real.

Acknowledgment

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Note added in proof. After completion of this work we noticed a recent paper containing mean amplitudes for biphenylene from electron diffraction: *A. Yokozeki, C. F. Wilcox,* Jr., and *S. H. Bauer,* J. Amer. Chem. Soc. **96**, 1026 (1974). The calculated mean amplitudes therein (based on spectral data from 1968) for $C_{12}H_8$ are all comparable with ours. The cited paper should be consulted for a comparison between the electron diffraction and spectroscopical data.

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