Normal Coordinate Analysis of Azulene

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A normal coordinate analysis was performed for azulene. A harmonic force field, potential energy distribution, and calculated mean amplitudes of vibration are reported. The results agree reasonably well with previously given electron diffraction mean amplitude values. The mean amplitudes of vibration are shortly discussed in relation to the partial aromatic character of azulene.

Several structural and spectral investigations on cyclic hydrocarbons have been reported in the last years. Davis and Muecke [1] have reported an electron diffraction study of cyclopentene, and Adams *et al.* [2] have performed similar work on cyclopentane. An investigation of spiropentane has been reported by Dallinga *et al.* [3] Electron diffraction works on the six-membered ring molecules cyclohexene, 1,3-cyclohexadiene, and 1,4-cyclohexadiene are reported by various authors. [4-8] Recently published spectral data and normal coordinate analysis for these three molecules are also available. [9-12] Hagen in his thesis [13] has thoroughly treated the structural aspects of 1,3-cycloheptadiene, bicyclo[4.1.0]-2-heptene and bicyclopropyl on the basis of gas electron diffraction works. Structural and spectroscopic data for 1,3-cycloheptadiene are also available. [14-15] Among the other cyclic hydrocarbons treated by electron diffraction are bicyclo[1.1.1]pentane, [16-18] bicyclo[2.1.0]pentane, [19] 1,3,5,7-cyclooctatetraene, [20-23] 1,3-cyclooctadiene, [24] and perylene. [25-26] Almenningen *et al.* [27] have reported an electron diffraction study on the aromatic molecules naphthalene, anthracene, and coronene. Spectroscopic calculations of mean amplitudes have been performed for benzene, [28] naphthalene, [29] and anthracene. [29] For benzene some earlier electron diffraction analyses are available. [20,30,31]

The azulene molecule has been investigated several times, both structurally [32] and spectroscopically. [33-36] In the present work a normal coordinate analysis is carried out for this molecule, and mean amplitudes of vibration are calculated. Some comments are finally given on the interesting correlation between the aromatic character of the molecule and the mean amplitudes of vibration.

SYMMETRY COORDINATES

According to Bastiansen and Derrisen [32] azulene possesses C_{2v} symmetry. Fig. 1 shows the molecular model. The following set of symmetry coordinates were constructed by the method described by Wilson *et al.*[37]
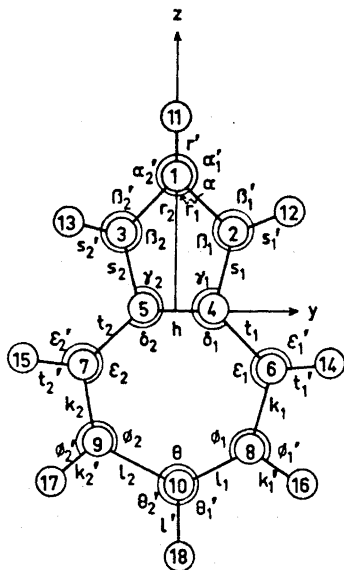

Fig. 1. Molecular model of azulene. In-plane valence coordinates are indicated. The out-of-plane coordinates (not indicated on the figure) are specified below in terms of the respective atom numbers. (i) Torsions: τ_{r1}(3-1-2-4), τ_{r2}(2-1-3-5), τ_{k1}(10-8-6-4), τ_{k2}(10-9-7-5), τ_{l1}(9-10-8-6), τ_{l2} (8-10-9-7); (ii) out-of-plane bendings: ξ_1(7,3-5-4), ξ_2(6,2-4-5), β_1''(4,1-2-12), β_2''(5,1-3-13), ε_1''(8,4-6-14), ε_2''(9,5-7-15), ϕ_1''(10,6-8-16), ϕ_2''(10, 7-9-17), α''(2,3-1-11), θ''(8,9-10-18). The capital letters R, S, R', S', *etc.*, are used to designate the appropriate equilibrium distances.

Species A_1:

$S_1 = 2^{-\frac{1}{2}} (r_1 + r_2)$, $S_2 = 2^{-\frac{1}{2}} (s_1 + s_2)$, $S_3 = 2^{-\frac{1}{2}} (t_1 + t_2)$

$S_4 = h$, $S_5 = 2^{-\frac{1}{2}} (k_1 + k_2)$, $S_6 = 2^{-\frac{1}{2}} (l_1 + l_2)$

$S_7 = (RS/2)^{\frac{1}{2}} (\beta_1 + \beta_2)$, $S_8 = (HT/2)^{\frac{1}{2}} (\delta_1 + \delta_2)$, $S_9 = (TK/2)^{\frac{1}{2}} (\varepsilon_1 + \varepsilon_2)$

$S_{10} = r'$, $S_{11} = 2^{-\frac{1}{2}} (s_1' + s_2')$, $S_{12} = 2^{-\frac{1}{2}} (t_1' + t_2')$

$S_{13} = 2^{-\frac{1}{2}} (k_1' + k_2')$, $S_{14} = l'$, $S_{15} = (RS/2)^{\frac{1}{2}} (\beta_1' + \beta_2')$

$S_{16} = (TT'/2)^{\frac{1}{2}} (\varepsilon_1' + \varepsilon_2')$, $S_{17} = (KK'/2)^{\frac{1}{2}} (\phi_1' + \phi_2')$

Species A_2:

$S_1 = (RS/2)^{\frac{1}{2}} (\tau_{r1} + \tau_{r2})$, $S_2 = (LT/2)^{\frac{1}{2}} (\tau_{k1} + \tau_{k2})$

$S_3 = (KL/2)^{\frac{1}{2}} (\tau_{l1} + \tau_{l2})$, $S_4 = [(RS)^{\frac{1}{2}} S'/2]^{\frac{1}{2}} (\beta_1'' + \beta_2'')$

$S_5 = [(KT)^{\frac{1}{2}} K'/2]^{\frac{1}{2}} (\varepsilon_1'' + \varepsilon_2'')$, $S_6 = [(LK)^{\frac{1}{2}} K'/2]^{\frac{1}{2}} (\phi_1'' + \phi_2'')$

Species B_1:

$S_1 = [(ST)^{\frac{1}{2}} H/2]^{\frac{1}{2}} (\xi_1 - \xi_2)$, $S_2 = (RS/2)^{\frac{1}{2}} (\tau_{r1} - \tau_{r2})$

$S_3 = (LT/2)^{\frac{1}{2}} (\tau_{k1} - \tau_{k2})$, $S_4 = (KL/2)^{\frac{1}{2}} (\tau_{l1} - \tau_{l2})$

$$S_5 = [(RS)^{\frac{1}{2}} S'/2]^{\frac{1}{2}} (\beta_1'' - \beta_2''), \quad S_6 = [(KT)^{\frac{1}{2}} T'/2]^{\frac{1}{2}} (\varepsilon_1'' - \varepsilon_2'')$$

$$S_7 = [(LK)^{\frac{1}{2}} K'/2]^{\frac{1}{2}} (\phi_1'' - \phi_2''), \quad S_8 = S = (RR')^{\frac{1}{2}} \alpha''$$

$$S_9 = (LL')^{\frac{1}{2}} \theta''$$

Species B_2:

$$S_1 = 2^{-\frac{1}{2}} (r_1 - r_2), \quad S_2 = 2^{-\frac{1}{2}} (s_1 - s_2), \quad S_3 = 2^{-\frac{1}{2}} (t_1 - t_2)$$

$$S_4 = 2^{-\frac{1}{2}} (k_1 - k_2), \quad S_5 = 2^{-\frac{1}{2}} (l_1 - l_2), \quad S_6 = (RS/2)^{\frac{1}{2}} (\beta_1 - \beta_2)$$

$$S_7 = (HT/2)^{\frac{1}{2}} (\delta_1 - \delta_2), \quad S_8 = (Tk/2)^{\frac{1}{2}} (\varepsilon_1 - \varepsilon_2), \quad S_9 = 2^{-\frac{1}{2}} (s_1' - s_2')$$

$$S_{10} = 2^{-\frac{1}{2}} (t_1' - t_2'), \quad S_{11} = 2^{-\frac{1}{2}} (k_1' - k_2'), \quad S_{12} = (RS'/2)^{\frac{1}{2}} (\beta_1' - \beta_2')$$

$$S_{13} = (TT'/2)^{\frac{1}{2}} (\varepsilon_1' - \varepsilon_2'), \quad S_{14} = (KK'/2)^{\frac{1}{2}} (\phi_1' - \phi_2')$$

$$S_{15} = (RR'/2)^{\frac{1}{2}} (\alpha_1' - \alpha_2'), \quad S_{16} = (LL'/2)^{\frac{1}{2}} (\theta_1' - \theta_2')$$

Table 1. Experimental frequencies of vibration (cm^{-1}) for azulene used in the present calculations.

A_1[a]	C−H stretching	3091	B_1[b]	C−H op[c] bend	1000
		3074			960
		3059			946
		3024			764
		3002			721
	C−C stretching			Ring op[c]	
	(arom.)	1638		deformation	664
		1580			492
		1443			311
		1392			165
	CCH ip[c] bend	1294			
		1117	B_2[a]	C−H stretching	3083
		1054			3044
	C−C stretching				3007
	(single bond)	899		C−C stretching	
	CCC ring bend	671		(arom.)	1694
		559			1580
		492			1479
		403			1453
				CCH ip[c] bend	1301
					1205
A_2[b]	C−H op[c] bend	1000			1151
		908			1007
		795			970
	Ring op[c]			CCC ring bend	721
	deformation	531			593
		323[d]			559
		163[d]			478

[a] From Ref. 34. [b] From Ref. 33. [c] ip= in plane, op= out of plane. [d] Calculated in Ref. 33.

STRUCTURAL AND SPECTRAL DATA

Bastiansen and Derrisen [32] report structural data for azulene, obtained by electron diffraction. Vibrational frequencies are given by Steele,[33,35] Hunt and Ross,[36] and van Tets and Günthard.[34] There are some small discrepancies between these works, and Table 1 shows the frequencies we have adopted for the computations in the present work. The in-plane vibrational frequencies, species A_1 and B_2, are taken from van Tets and Günthard,[34] taking into consideration the assignment of Steele.[35] All out-of-plane frequencies are from Ref. 33.

FORCE FIELD AND POTENTIAL ENERGY DISTRIBUTION

The harmonic force field for azulene was arrived at through several iterations. In Table 2 the final force constants are given which reproduce the vibrational frequencies exactly. Some of the force constants in Table 2 might seem astonishingly great. However, they are understandable in wiew of the theory of redundant symmetry coordinates described by Cyvin and Cyvin.[38] Table 3 gives the approximate description of the normal modes according to the calculated potential energy distribution terms. Compared to the experimental assignment of frequencies (Table 1) there are a few discrepancies.

Table 2. Symmetry force constants (in mdyne/Å) for azulene.

									Species A_1
1	7.320								
2	0.207	6.613							
3	−0.359	−0.529	7.828						
4	−0.440	−0.543	2.393	7.507					
5	−0.078	−0.315	−1.045	−1.670	7.055				
6	0.010	0.147	−3.905	−4.844	2.037	12.031			
7	−0.227	−0.059	−0.059	−0.174	0.118	0.115	0.641		
8	−0.242	−0.977	6.825	8.581	−3.415	−11.358	−0.364	23.102	
9	−0.114	−0.451	4.135	4.956	−1.813	−6.716	−0.139	13.225	8.313
10	−0.121	0.0531	−0.043	−0.006	0.006	0.009	−0.035	−0.052	−0.023
11	−0.050	−0.084	−0.027	−0.019	−0.041	−0.004	0.048	−0.012	−0.007
12	−0.020	−0.045	−0.101	0.037	−0.119	−0.006	−0.001	0.071	0.074
13	−0.014	−0.048	−0.063	−0.122	−0.012	0.070	−0.003	−0.213	−0.144
14	0	0.010	0.035	0.024	0.025	−0.092	0.005	0.126	0.087
15	−0.015	−0.075	0.085	0.074	0.029	0.013	−0.031	0.036	0.030
16	−0.035	−0.092	0.012	−0.021	−0.067	0.004	0.018	−0.094	−0.046
17	−0.042	−0.053	0.131	0.007	0.018	−0.177	−0.004	0.187	0.126
10	5.086							Species A_1	
11	0.041	5.115						(continued)	
12	−0.007	0.002	5.070						
13	0	−0.003	−0.055	4.973					
14	0	−0.001	0.018	−0.029	4.912				
15	0.013	−0.011	0.002	0.005	0.001	0.582			
16	0	−0.012	−0.016	−0.004	0.001	0.004	0.599		
17	−0.005	−0.003	0.018	−0.006	−0.010	0.012	0.032	0.595	

Table 2. Continued.

Species A_2

1	0.773					
2	−0.117	1.001				
3	−0.154	1.673	3.177			
4	−0.015	−0.046	−0.085	0.219		
5	0.020	0.009	−0.002	−0.010	0.192	
6	0.024	−0.016	−0.004	0.006	0.013	0.208

Species B_1

1	0.320								
2	0.005	0.130							
3	−0.035	−0.018	0.195						
4	−0.041	−0.005	0.027	0.157					
5	0.031	−0.023	0.008	−0.006	0.223				
6	0.035	−0.011	0.043	−0.026	0.009	0.244			
7	−0.016	0.004	−0.043	0.053	−0.003	−0.009	0.220		
8	−0.003	0.018	−0.006	−0.002	0.005	0.003	0.004	0.217	
9	−0.020	0.002	−0.027	0.053	−0.009	0.001	0.009	0.001	0.227

Species B_2

1	8.482							
2	3.619	11.463						
3	1.050	1.583	8.241					
4	0.450	0.528	1.163	7.217				
5	0.112	0.094	0.182	0.701	6.297			
6	2.421	3.566	1.057	0.580	0.099	2.964		
7	−0.744	−1.438	0.394	0.008	−0.128	−0.668	1.466	
8	−0.040	−0.444	1.103	0.645	0.005	0.059	0.877	1.603
9	−0.151	−0.102	0.001	−0.034	−0.006	0.006	−0.013	−0.026
10	0.005	0.040	−0.043	−0.050	0.073	0.003	−0.026	−0.003
11	0.014	−0.020	0.087	−0.019	−0.108	0.255	0.020	0.030
12	−0.083	−0.107	0.042	0.080	0.005	−0.095	0.055	0.061
13	0.068	0.137	0.217	0.135	0.044	0.059	−0.006	0.015
14	0.022	0.041	−0.028	−0.036	−0.097	0.225	−0.066	−0.034
15	0.216	0.096	0.008	0.020	0.012	0.026	−0.020	−0.014
16	0.020	0.033	0.015	0.033	0.144	0.021	−0.006	0.007

Species B_2 (continued)

9	5.125							
10	0.068	5.008						
11	−0.003	−0.040	4.925					
12	−0.001	−0.003	0.007	0.360				
13	−0.001	0.003	0.009	−0.033	0.336			
14	0	0.004	−0.010	0.007	0.038	0.374		
15	0.023	0.002	0.001	0.006	0.004	0.001	0.347	
16	0.001	0	0.013	0.007	0.014	−0.005	−0.003	0.352

Table 3. Approximate description of normal modes and potential energy distribution for azulene.

Symm	Fre., cm^{-1}.		
A_1	3091	C−H stretching	$(31r' + 66s')$
	3074	C−H stretching	$(77t' + 16k')$
	3059	C−H stretching	$(65r' + 31s')$
	3024	C−H stretching	$(19t' + 66k' + 14l')$
	3002	C−H stretching	$(16k' + 83l')$
	1638	C−C stretching	$(20s + 44t + 33k + 34\delta + 11\varepsilon')$
	1580	C−C stretching	$(16r + 29s + 18k + 24\beta')$

Table 3. Continued.

	1443	CCC bend	$(33t + 51h + 19l + 92\delta + 102\varepsilon + 19\phi')$
	1392	C—C stretching, CCC bend	$(15r + 19h + 18l + 57\delta + 10\beta' + 21\varepsilon' + 23\phi')$
	1294	C—C stretching, CCC bend	$(17r + 23s + 10\varepsilon' + 17\phi')$
	1117	C—C stretching, CCC bend	$(11r + 11k + 10l + 32\varepsilon' + 19\phi')$
	1054	CCH ip [a] bend	$(33r + 12\delta + 43\beta')$
	899	C—C stretching	$(13k + 98l + 60\delta)$
	671	CCC bend	$(128\delta + 466\varepsilon)$
	559	C—C stretching, CCC bend	$(35t + 71h + 18l + 15\beta + 20\delta)$
	492	CCC bend	$(12t + 74\beta + 106\delta + 52\varepsilon)$
	403	CCC bend	$(739\delta + 514\varepsilon)$
A_2	1000	Ring torsion, CCH op [a] bend	$(172\tau_k + 108\tau_l + 49\varepsilon'' + 35\phi'')$
	908	CCH op [a] bend	$(13\tau_l + 58\beta'' + 21\phi'')$
	795	CCH op [a] bend	$(27\beta'' + 28\varepsilon'' + 39\phi'')$
	531	Ring torsion, CCH op [a] bend	$(22\tau_r + 30\tau_k + 14\beta'' + 21\varepsilon'')$
	323	Ring torsion	$(653\tau_k + 701\tau_l)$
	163	Ring torsion	$(65\tau_r + 27\tau_l)$
B_1	1000	Ring op [a] deformation, CCH op [a] bend	$(42\tau_k + 63\tau_l + 22\varepsilon'' + 58\phi'' + 42\theta'')$
	960	CCH op [a] bend	$(18\tau_r + 53\beta'' + 40\alpha'')$
	946	CCH op [a] bend	$(64\varepsilon'' + 26\theta'')$
	764	CCH op [a] bend	$(35\beta'' + 47\alpha'')$
	721	CCH op [a] bend	$(14\varepsilon'' + 46\phi'' + 32\theta'')$
	664	Ring op [a] deformation	$(11\xi + 24\tau_k + 23\tau_l)$
	492	Ring op [a] deformation	$(48\xi + 18\tau_r + 24\tau_l)$
	311	Ring op [a] deformation	$(20\xi + 65\tau_r + 11\tau_k)$
	165	Ring op [a] deformation	$(13\xi + 47\tau_k + 14\tau_l)$
B_2	3083	C—H stretching	$(98s')$
	3044	C—H stretching	$(84t' + 14k')$
	3007	C—H stretching	$(15t' + 84k')$
	1694	C—C stretching	$(41s + 37t + 23k + 17l + 23\delta)$
	1580	C—C stretching	$(25s + 59l + 11\theta')$
	1479	C—C stretching	$(86r + 21\beta + 35\alpha')$
	1453	C—C stretching	$(39s + 34k + 21\theta')$
	1301	C—C stretching, CCH ip [a] bend	$(11s + 28t + 37\theta')$
	1205	Ring ip [a] bend, CCH ip [a] bend	$(25r + 11s + 18\beta + 12\delta + 47\alpha')$
	1151	Ring ip [a] bend, CCH ip [a] bend	$(12t + 14k + 13l + 18\varepsilon' + 22\theta')$
	1007	CCH ip [a] bend	$(16\delta + 12\varepsilon + 58\beta' + 12\phi')$
	970	CCH ip [a] bend	$(18\varepsilon' + 56\phi')$
	721	CCH ip [a] bend, ring ip [a] bend	$(13s + 18k + 12\beta + 22\beta' + 56\varepsilon' + 16\phi')$
	593	Ring ip [a] bend	$(25s + 81\beta + 71\delta + 92\varepsilon)$
	559	Ring ip [a] bend	$(24\beta + 38\varepsilon)$
	478	Ring ip [a] bend	(42δ)

[a] ip = in plane, op = out of plane.

Table 4. Mean amplitudes of vibration, u, (Å units), for azulene.

Distance type $(i-j)^a$		(Equil. dist. in Å)	u spectr.		u electr. diff. Ref. 29
			0 K	298 K	
C – H	(1 – 11)	(1.085)	0.0770	0.0770	
C – H	(2 – 12)	(1.085)	0.0769	0.0769	
C – H	(6 – 14)	(1.085)	0.0772	0.0772	0.090
C – H	(8 – 16)	(1.085)	0.0776	0.0776	
C – H	(10 – 18)	(1.085)	0.0777	0.0777	
C – C	(1 – 2)	(1.399)	0.0447	0.0448	0.0486
C – C	(2 – 4)	(1.418)	0.0442	0.0445	
C – C	(4 – 5)	(1.501)	0.0488	0.0497	
C – C	(4 – 6)	(1.383)	0.0446	0.0451	
C – C	(6 – 8)	(1.406)	0.0445	0.0448	
C – C	(8 – 10)	(1.403)	0.0451	0.0454	
C···C	(1 – 4)	(2.290)	0.0569	0.0603	
C···C	(1 – 6)	(3.624)	0.0608	0.0652	
C···C	(1 – 8)	(4.780)	0.0648	0.0705	
C···C	(1 – 10)	(5.203)	0.0670	0.0741	
C···C	(2 – 6)	(2.487)	0.0553	0.0584	
C···C	(2 – 8)	(3.808)	0.0598	0.0639	
C···C	(2 – 10)	(4.548)	0.0636	0.0694	
C···C	(2 – 9)	(4.509)	0.0618	0.0657	
C···C	(2 – 7)	(3.685)	0.0594	0.0623	
C···C	(2 – 5)	(2.335)	0.0551	0.0572	
C···C	(2 – 3)	(2.292)	0.0575	0.0604	0.054
C···C	(4 – 8)	(2.499)	0.0542	0.0567	
C···C	(4 – 10)	(3.130)	0.0608	0.0658	0.078
C···C	(4 – 9)	(3.172)	0.0601	0.0637	
C···C	(4 – 7)	(2.599)	0.0571	0.0596	
C···C	(6 – 10)	(2.537)	0.0554	0.0571	0.057
C···C	(6 – 9)	(3.190)	0.0641	0.0687	
C···C	(6 – 7)	(3.227)	0.0664	0.0723	
C···C	(8 – 9)	(2.542)	0.0584	0.0614	
C···H	(1 – 12)	(2.212)	0.1007	0.1033	
C···H	(1 – 14)	(4.029)	0.1334	0.1379	
C···H	(1 – 16)	(5.703)	0.1080	0.1116	
C···H	(1 – 18)	(6.288)	0.0989	0.1040	
C···H	(2 – 11)	(2.208)	0.0975	0.0981	
C···H	(2 – 14)	(2.688)	0.1373	0.1420	
C···H	(2 – 16)	(4.598)	0.1127	0.1155	
C···H	(2 – 18)	(5.604)	0.0984	0.1024	
C···H	(2 – 17)	(5.550)	0.0979	0.1003	
C···H	(2 – 15)	(4.414)	0.1179	0.1207	
C···H	(2 – 13)	(3.335)	0.0934	0.0947	
C···H	(4 – 11)	(3.335)	0.0942	0.0966	
C···H	(4 – 12)	(2.231)	0.1055	0.1074	
C···H	(4 – 13)	(3.390)	0.0955	0.0976	
C···H	(4 – 14)	(2.103)	0.1048	0.1057	
C···H	(4 – 16)	(3.416)	0.0998	0.1010	
C···H	(4 – 18)	(4.192)	0.0961	0.0995	
C···H	(4 – 17)	(4.242)	0.0948	0.0970	
C···H	(4 – 15)	(3.528)	0.1015	0.1030	
C···H	(6 – 16)	(2.113)	0.1051	0.1059	
C···H	(6 – 18)	(3.444)	0.0998	0.1008	
C···H	(6 – 17)	(4.250)	0.0997	0.1032	
C···H	(6 – 15)	(4.293)	0.0987	0.1025	

Table 4. Continued.

C⋯H	(6 − 13)	(4.708)	0.1019	0.1049
C⋯H	(6 − 11)	(4.621)	0.0996	0.1029
C⋯H	(6 − 12)	(2.858)	0.1345	0.1394
C⋯H	(8 − 18)	(2.106)	0.1013	0.1017
C⋯H	(8 − 17)	(3.448)	0.1085	0.1111
C⋯H	(8 − 15)	(4.254)	0.0997	0.1035
C⋯H	(8 − 13)	(5.403)	0.1136	0.1178
C⋯H	(8 − 11)	(5.834)	0.0991	0.1032
C⋯H	(8 − 12)	(4.263)	0.1360	0.1414
C⋯H	(8 − 14)	(2.123)	0.1118	0.1140
C⋯H	(10 − 11)	(6.288)	0.0987	0.1038
C⋯H	(10 − 12)	(5.232)	0.1281	0.1340
C⋯H	(10 − 14)	(3.455)	0.1068	0.1091
C⋯H	(10 − 16)	(2.110)	0.1107	0.1126
H⋯H	(11 − 12)	(2.653)	0.1597	0.1616
H⋯H	(11 − 14)	(4.894)	0.1644	0.1692
H⋯H	(11 − 16)	(6.723)	0.1351	0.1384
H⋯H	(11 − 18)	(7.373)	0.1226	0.1268
H⋯H	(12 − 14)	(2.622)	0.1952	0.2024
H⋯H	(12 − 16)	(4.858)	0.1790	0.1843
H⋯H	(12 − 18)	(6.236)	0.1538	0.1593
H⋯H	(12 − 17)	(6.472)	0.1340	0.1374
H⋯H	(12 − 15)	(5.484)	0.1392	0.1420
H⋯H	(12 − 13)	(4.339)	0.1219	0.1224
H⋯H	(14 − 16)	(2.353)	0.1852	0.1901
H⋯H	(14 − 18)	(4.227)	0.1487	0.1510
H⋯H	(14 − 17)	(5.299)	0.1286	0.1321
H⋯H	(14 − 15)	(5.347)	0.1230	0.1257
H⋯H	(16 − 18)	(2.328)	0.1693	0.1715
H⋯H	(16 − 17)	(4.215)	0.1519	0.1549

MEAN AMPLITUDES OF VIBRATION

Table 4 shows the calculated mean amplitudes of vibration (u) at absolute zero and 298 K, along with the observed values from electron diffraction. No serious discrepancies between observed and calculated u values are found.

Table 5. Bond lengths, r, and mean amplitudes of vibration, u, (Å units) of bonded carbon-carbon atom pairs in some cyclic hydrocarbons at 298 K.

Molecule	C = C double bond		CC aromatic		C − C single bond	
	r	u	r	u	r	u
Benzene[a]			1.397	0.0461		
1,4-Cyclohexadiene [b]	1.334	0.0419			1.496	0.0475
1,3-Cyclohexadiene [b]	1.348	0.0427			1.465	0.0484
					1.519	0.0478
					1.538	0.0482
Azulene			1.383	0.0451	1.501	0.0497
			1.399	0.0448		
			1.403	0.0454		
			1.406	0.0448		
			1.418	0.0445		

[a] From Ref. 28.   [b] From Ref. 12.

Carbon-carbon bond lengths and corresponding u values for some cyclic hydrocarbons are shown in Table 5. It is seen that a clear correlation exists between the bond length, mean amplitude of vibration, and the type of carbon-carbon bond (*e.g.* double bond, aromatic bond, single bond). Single-bond u values lie around $0.048-0.050$ Å, double-bond values around 0.042 Å, whereas aromatic carbon-carbon u values lie in between these limits, around $0.045-0.046$ Å. The bond $4-5$ (Fig. 1) of azulene has typical single-bond values of r and u, and all the other carbon-carbon bond lengths and mean amplitudes are typical for aromatic molecules.

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