Perpendicular Amplitude Correction Coefficients for 1,3-Butadiene from Spectroscopic Data

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Recently the mean amplitudes of vibration [1] (u) for 1,3-butadiene have been calculated from spectroscopic data [2] and compared with electron diffraction values. The similar work [3] on *cis* and *trans* 1,3,5-hexatriene also includes the calculated perpendicular amplitude correction coefficients [1] (K). These quantities are (in common with the mean amplitudes) of great interest in modern interpretations of gas electron diffraction measurements. In Table 1 the calculated results of K values for 1,3-butadiene are presented. They were obtained from the harmonic force field previously used in the mean amplitude calculations.[2] The interatomic distances are given (see Table 1) in the same sequence as in Table 2 of the cited work,[2] and approximate equilibrium separations (r_e in Å units) are included in parentheses.

Table 1. 1,3-Butadiene: Calculated perpendicular amplitude correction coefficients (Å units).

Distance	(equil.)	$T=0$	298°K
C_1-H_1	(1.094)	0.0179	0.0198
C_1-H_1'	(1.094)	0.0219	0.0288
C_2-H_2	(1.094)	0.0168	0.0204
$C_1=C_2$	(1.344)	0.0036	0.0065
C_2-C_3	(1.467)	0.0014	0.0015
$C_1\cdots C_3$	(2.469)	0.0017	0.0032
$C_1\cdots C_4$	(3.695)	0.0002	0.0002
$C_2\cdots H_1$	(2.110)	0.0104	0.0131
$C_2\cdots H_1'$	(2.110)	0.0135	0.0228
$C_1\cdots H_2$	(2.110)	0.0106	0.0173
$C_2\cdots H_3$	(2.201)	0.0074	0.0093
$C_3\cdots H_1$	(3.456)	0.0059	0.0075
$C_3\cdots H_1'$	(2.692)	0.0096	0.0165
$C_1\cdots H_3$	(2.709)	0.0075	0.0127
$C_1\cdots H_4$	(4.577)	0.0034	0.0038
$C_1\cdots H_4'$	(4.031)	0.0042	0.0058
$H_1\cdots H_1'$	(1.905)	0.0247	0.0320
$H_1\cdots H_2$	(2.422)	0.0151	0.0209
$H_1'\cdots H_2$	(3.081)	0.0155	0.0277
$H_2\cdots H_3$	(3.151)	0.0087	0.0092
$H_1\cdots H_3$	(3.798)	0.0094	0.0131
$H_1'\cdots H_3$	(2.469)	0.0185	0.0331
$H_1\cdots H_4$	(5.536)	0.0050	0.0052
$H_1'\cdots H_4$	(4.724)	0.0071	0.0091
$H_1'\cdots H_4'$	(4.610)	0.0054	0.0058

It is intended to use these K values along with those of hexatrienes [2] in refined structure studies of hydrocarbons with conjugated double bonds in connection with the systematic electron diffraction investigations of such molecules.[4] When the K values are known it is possible to derive the average structure [5] with the aid of the relation

$$r_\alpha = r_g(1) + (u^2/r_e) - K \qquad (1)$$

The angles $\theta\alpha$ of the average structure may be determined from the bonded and nonbonded r_α distances by Euclidean geometry. Thus the incorporation of K values according to eqn. (1) into a least-squares refinement of electron diffraction measurements should theoretically improve the exploitation of the material in a rational way.

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