Vibrational modes and force constants of *p*-bromotoluene

S. A. Katsyuba

A. E. Arbuzov Institute of Organic and Physical Chemistry, Kazan' Scientific Center of the Russian Academy of Sciences,
8 ul. Akad. Arbuzova, 420083 Kazan', Russian Federation.
Fax: 007 (843 2) 75 2253. E-mail: litvinov@glass.ksu.ras.ru

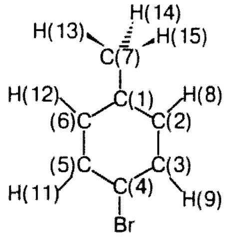
The characteristic features of the normal vibrational modes of *p*-bromotoluene were calculated; the assignments of spectral bands reported previously were corrected. The force constants of the molecule were estimated in terms of the model of the unified valence and force field.

Key words: *p*-bromotoluene, vibrational spectra, force constants.

The normal vibrational modes of alkyl- and halobenzenes have been analyzed by a number of researchers (see, for example, Refs. 1—4). The present study is the first attempt to interpret theoretically the spectra of benzene derivatives simultaneously containing both types of substituents.

Calculation procedure

All calculations were carried out using published programs.[5] Initially, the IR spectrum of toluene was calculated based on the parameters[4] included in the library of the program package.[5] This led to substantial (up to 50 cm^{-1}) deviations of some calculated frequencies from their experimental values.[1] To remove these discrepancies, the following changes were introduced into the initial force field:[4] the force constant of the C(1)—C(7) bond and the constants for its interaction with the carbon—carbon bond of the aromatic ring as well as with the C(2)C(1)C(6) angle were taken from the literature,[2] and the $K_{C(2)C(1)C(7)}$ parameter was taken to be 1.033 (from here on, the previously accepted designations[6] and 10^6 cm^{-2} units are used for force constants). The resulting potential field, together with parameters K_{CBr}, K_{CCBr}, $H^{CBr}_{C(3)C(4)}$, and $A^{C(3)C(4)Br}_{C(3)C(4)}$ transferred from the force field of bromobenzene,[3] were used as the zero approximation in calculation of the frequencies and modes of normal vibrations of *p*-bromotoluene (**1**). The geometric characteristics used for **1** were the same as those in the toluene molecule (except for the length of the C—Br bond, which was taken as being equal to 1.9 Å, as in the bromobenzene molecule[7]); for hydrogen atoms, spectroscopic magnitudes of the weight (1.088 amu) were used.[6] The torsion vibrations of the methyl group were not calculated.



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Results and Discussion

Despite the fact that the equilibrium configuration of molecule **1** used in the calculations has C_s symmetry, its experimental vibrational spectra can be interpreted based on C_{2v} symmetry, which would correspond to this molecule if the methyl radical was monoatomic.[8] The spectra exhibit 11a$_1$ + 10b$_2$ in-plane and 3a$_2$ + 6b$_1$ out-of-plane vibrations of the aromatic fragment. The frequencies of the in-plane vibrations, calculated with a force field in the zero approximation, are in satisfactory agreement with the experimental results[8] (Table 1). However, some of the theoretical frequencies of the out-of-plane vibrations deviate markedly from the corresponding measured values.[8] Therefore, the initial values of some force constants were varied in such a way that the discrepancies between the calculated and experimental frequencies would not exceed the errors of the measurements. Derivatives of the frequencies with respect to the force constants were used.[6] As a result, the following values were obtained for the variable parameters of the potential field of the molecule:

$$\rho^{C(2)C(1)C(6)}_{C(1)C(7)} = 0.653,\ \rho^{C(1)C(2)C(3)}_{C(2)H} = 0.615,$$

$$\rho^{C(2)C(3)C(4)}_{C(3)H} = 0.510,\ \rho^{C(3)C(4)C(5)}_{CBr} = 0.820,$$

$${}^{C(3)C(4)C(5)}_{C(2)C(3)C(4)}\delta^{C(2)C(1)C(6)}_{C(1)C(7)} = 0,$$

$${}^{C(2)C(3)C(4)}_{C(3)H}\phi^{C(1)C(2)C(3)}_{C(2)H} = 0.030,$$

$${}^{C(5)C(6)C(1)}_{C(6)H}\phi^{C(1)C(2)C(3)}_{C(2)H} = -0.100,$$

$${}^{C(2)C(3)C(4)}_{C(1)C(2)C(3)}\delta^{C(1)C(2)C(3)}_{C(2)H} = 0.112,$$

$${}^{C(3)C(4)C(5)}_{CBr}\phi^{C(2)C(3)C(4)}_{C(3)H} = -0.016,$$

$${}^{C(4)C(5)C(6)}_{C(5)H}\phi^{C(2)C(3)C(4)}_{C(3)H} = -0.042.$$

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Table 1. Characteristics of the vibrational spectrum of compound **1**

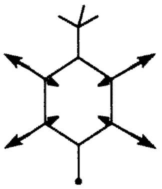
Experiment[a]			Calculation		
No.	ν/cm^{-1}	Type of symmetry	ν/cm^{-1}	Distribution of potential energy (%)[b]	No. according to Wilson
1	3060	a_1	3067	99ν(CH)	
2	3060	a_1	3059	99ν(CH)	
21	3038	b_2	3064	99ν(CH)	*20b*
22	3025	b_2	3056	99ν(CH)	*7b*
	2974		2968	100ν_{as}(CH$_3$)	
	2951		2967	100ν_{as}(CH$_3$)	
	2924		2894	100ν_s(CH$_3$)	
3	1590	a_1	1618	78ν(CC), 12δ(CH)	*8a*
23	1579	b_2	1627	81ν(CC)	*8b*
4	1488	a_1	1508	58δ(CH), 33ν(CC)	*19a*
	1449		1460	82δ_{as}(CH$_3$)	
	1449		1459	90δ_{as}(CH$_3$)	
24	1397	b_2	1382	56ν(CC), 26δ(CH)	*19b*
	1379		1383	92δ_s(CH$_3$)	
25	1299	b_2	1307	74δ(CH), 24ν(CC)	*3*
26	1270	b_2	1298	78ν(CC), 21δ(CH)	*14*
5	1210	a_1	1216	50ν(C—CH$_3$), 24ν(CC), 123δ(CH)	
6	1177	a_1	1180	94δ(CH)	*9a*
27	1112	b_2	1111	49δ(CH), 35ν(CH)	*15*
7	1069	a_1	1091	54ν(CC), 21ν(CBr), 14δ(CCC)	
	1040		1031	72ρ(CH$_3$)	
8	1012	a_1	1015	40δ(CCC), 39ν(CC), 17δ(CH)	*18a*
			971	72ρ(CH$_3$), 16ν(CC)	
12	956	a_2	960	97γ(CH^o)	
15	935	b_1	925	46τ, 36γ(CBr), 11γ(CH^o)	
13	815	a_2	818	96γ(CH^m)	
16	801	b_1	810	83γ(CH^o)	*10b*
9	793	a_1	789	34ν(CC), 32ν(C—CH$_3$), 21δ(CCC)	*1*
17	692	b_1	701	74γ(CH^m)	
28	635	b_2	619	70δ(CCC), 21δ(CH)	*6b*
10	590	a_1	591	38δ(CCC), 30ν(CBr)	*6a*
18	476	b_1	493	38γ(CH^m), 37τ	*16b*
14	405	a_2	408	64τ, 22γ(CH^m), 14γ(CH^o)	*16a*
29	364	b_2	372	68δ(C—CH$_3$), δ(CBr)	
11	292	a_1	290	65ν(CBr), 19δ(CCC)	
19	292	b_1	277	54γ(C—CH$_3$), 20γ(CBr)	*4*
30	216	b_2	209	74δ(CBr), 15δ(C—CH$_3$)	
20	121	b_1	94	34τ, 33γ(CH^m), 16γ(CBr), 13γ(C—CH$_3$)	

[a] See Ref. 8. The frequencies were averaged over the IR and Raman spectra. The numbers and types of symmetry are given only for vibrations of the aromatic ring. [b] Types of vibrations: ν, stretching; δ, deformation; τ, torsional of the aromatic ring; ρ, rocking; s, symmetrical; as, asymmetrical; γ(CH^o) are the deviations of the C(2)H(8) and C(6)H(12) bonds from the plane of the aromatic ring, γ(CH^m) are the corresponding vibrations of the C(3)H(9) and C(5)H(11) bonds. Contributions larger than 10% are presented.

The resulting force constants can be used for theoretical analysis and prediction of the vibrational spectra of *p*-bromo-substituted alkylbenzenes. The interpretation of the spectra of **1** based on these results is presented in Table 1.

The empirical assignments of bands and lines in the spectra of compound **1** suggested previously[8] were based on their correlation with the corresponding vibration frequencies of benzene (**2**). We had the opportunity to not only compare vibration frequencies but also the vibrational modes of both molecules. For this purpose, we constructed images for the shifts of the atoms during vibrations of molecule **1** and compared the results obtained with the similar graphic representation of the normal modes of **2**.[2] We found that many vibrational modes of molecule **1** are very similar to those of the corresponding vibrations of **2**. Obviously, the use of generally accepted designations of the normal modes of **2**, proposed by Wilson,[9] is legitimate only for these vibrations (these designations are presented in the last column of Table 1 and are indicated in italics in the text).

In view of the above, we believe that the previously reported[8] interpretation of bands No. 1 and 2 as being caused by Wilson types *2* and *20a* vibrations, respectively, was not quite correct. Using the graphic representation of the vibrations in question, we can easily see that the C(1) and C(4) atoms and the exocyclic groups attached to them are almost fixed, whereas the corresponding atoms in molecule **2** are substantially displaced during vibrations No. *2* and *20a*.[4] A similar juxtaposition of the representations of modes No. 12, 13, 15, and 17, which are presented below for clarity, with the corresponding graphic representations of the normal modes of **2** (see Ref. 2) indicates that the Wilson designations proposed for these vibrations[8] cannot be accepted either. Vibrations No. 12 and 13 are combinations of vibrations *10a* and *17a*, while vibrations No. 15 and 17 are combinations of vibrations *5* and *11* in molecule **2**.



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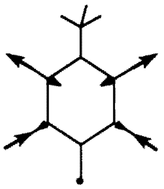

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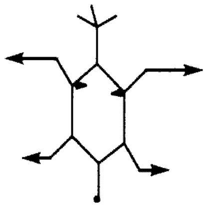

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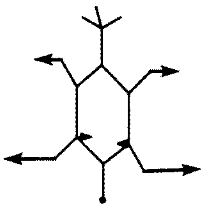

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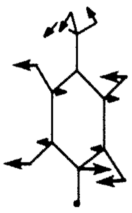
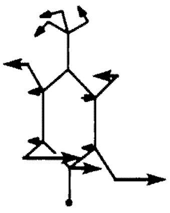


No. 15 (925)



No. 17 (701)

Conversely, vibrations No. 9, 10, and 19, although they are "X-sensitive",[10] can be classified as Wilson vibrations *1*, *6a*, and *4*, respectively, in full agreement with the previously reported[8] assignment, since they are close to the latter in their modes. At the same time, the assignment[7] of Wilson No. *4* to the band at 692 cm^{-1} (No. 17 in Table 1) was probably incorrect. Although vibration No. *4* in the spectra of toluene[1,2] and bromobenzene[3] is actually exhibited at ~690 cm^{-1}, deuteration of both molecules in the *para*-position decreases the corresponding frequency to ~600 cm^{-1}. Such great dependence on the weights of both *para*-substituents is due to the fact that the latter make the predominant contributions to this vibration (see Ref. 2 and Table 1). Since in molecule **1** the *para*-substituents are much heavier than deuterium, we should expect that vibration No. *4* would be exhibited at a markedly lower frequency than those in the case of any of the above molecules. Therefore, relying on the analysis of the forms of the vibrations, band No. 19 (292 cm^{-1}) was assigned to the vibration in question.

A similar comparison of frequencies and forms of the normal modes of molecules **1**, **2**,[2] toluene,[2] bromobenzene,[3] and their deuterated derivatives[1,3] showed that the assignments[8] of bands No. 6, 7, and 16 (see Table 1) need to be corrected.

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