

VIBRATIONAL SPECTRUM OF *o*-AMINO-BENZENETHIOL

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THE vibrational spectrum both Raman and infra-red, of *o*-amino-benzenethiol, has been investigated and the assignments of the different frequencies have been attempted on a close analogy with that for benzenethiol¹ and other substituted benzenes.^{2,3} The infra-red spectra have

dispersion of 19 Å/mm. in the λ 4358 region and a Hilger Raman Source Unit. The Raman and infra-red spectra, and the estimates of intensity in the conventional manner are given in Table I. The vibration types—class and mode—have been designated according to Wilsons' notation.⁴

TABLE I
Vibrational assignments of *o*-Amino benzenethiol

Frequency in cm. ⁻¹			Tentative Assignments		
Raman	Infra red		Class	Mode	
In liquid	Liquid	In CCl ₄			
172 (8)	B ₂	16 <i>b</i>	X sensitive vibrations of C ₆ H ₅ X
264 (8)	B ₂	11	
373 (6)	B ₁	16 <i>a</i>	
479 (6)	A ₁	6 <i>a</i>	
678 (9)	674 (w)	674 (w)	A ₁	12	
1093 (5)	A ₁	7 <i>a</i>	
561 (8)	B ₁	6 <i>b</i>	In-plane ring deformation (606 cm. ⁻¹ in benzene)
693 (1)	B ₂	4	Out-of-plane ring deformation
751 (6)	746 (s)	741 (s)	B ₂	10 <i>b</i>	Out-of-plane C—H deformations
834 (9)	844 (w)	840 (sh)	A ₂	10 <i>a</i>	
..	932 (w)	932 (m)	B ₂	17 <i>b</i>	
..	..	968 (m)	A ₂	17 <i>a</i>	
..	1084 (m)	1086 (s)	B ₂	5	
909 (5)	905 (m)	907 (s)	C—S—H in-plane deformation
1023 (10)	1024 (m)	1024 (s)	A ₁	18 <i>a</i>	In-plane C—H deformation
1154 (5)	1155 (m)	1155 (s)	B ₁	9 <i>b</i>	
..	1139 (w)	1139 (m)	A ₁	9 <i>a</i>	
1261 (6)	1250 (w)	1250 (m)	B ₁	3	
1302 (8)	1299 (s)	1299 (vs)	B ₁	14	C=C stretching
..	1447 (s)	1449 (s)	B ₁	19 <i>b</i>	
1484 (4)	1481 (s)	1479 (s)	A ₁	19 <i>a</i>	
1581 (9)	B ₁	8 <i>a</i>	
1606 (9)	1610 (s)	1608 (s)	A ₁	8 <i>b</i>	
..	..	1625 (sh)	N—H in plane deformation
2533 (7)	2510 (m)	2538 (s)	S—H stretching in <i>cis</i>
..	..	2600 (m)	S—H stretching in <i>trans</i>
3048 (7)	3030 (w)	3030 (m)	B ₁	7 <i>b</i>	C—H stretch
3071 (7)	3067 (w)	3067 (w)	A ₁	2	
3350 (5)	3338 (s)	3361 (s)	N—H symmetric stretch
..	3419 (s)	3460 (s)	N—H asymmetric stretch

N.B.—s = strong, vs = very strong, m = medium, sh = shoulder, w = weak. Concentration for the IR spectrum in CCl₄ is not given because the change in concentration has made no variation in frequency.

been recorded with a Model 21 Perkin-Elmer Double Beam IR spectrophotometer with NaCl optics, and the Raman spectrum has been recorded with a Fuess Glass Spectrograph, with a

In the Raman spectrum the S—H stretching frequency appears as a broad intense band extending from 2516 to 2550 cm.⁻¹ The line at 909 cm.⁻¹ can be assigned to C—S—H in-plane

deformation. In the infra-red the corresponding frequencies appear as a weak broad band at 2510 cm.^{-1} and another at 905 cm.^{-1} respectively. In solutions of CCl_4 the S—H stretching frequency in the infra-red shifts to 2538 cm.^{-1} . Josien *et al.*^{5,6} have observed a shift of this order in benzenethiol and other monohalogen benzenethiols. The frequency in solution, in these cases, corresponds to the frequency of benzenethiol vapour (2592 cm.^{-1}). Hence the shift in frequency while going from pure liquid state to the dilute CCl_4 solution has been explained as due to the breaking of the intermolecular association. Accordingly the liquid frequency at 2510 cm.^{-1} and the frequency in CCl_4 at 2538 cm.^{-1} can be assigned to the bonded and free S—H stretching frequency in *o*-amino-benzenethiol.

In addition to this in solutions of CCl_4 another band appears at 2600 cm.^{-1} which is comparable in intensity with the one at 2538 cm.^{-1} . These two bands do not show any relative variation in intensity with concentration. Josien *et al.* have observed a weak band in *o*-chloro, and *o*-bromo benzenethiols, below the S—H frequency and 2552 cm.^{-1} and 2545 cm.^{-1} respectively. In the *meta* and *para*-isomers no such band was reported.

The presence of this band at 2600 cm.^{-1} in the vicinity of the S—H band at 2538 cm.^{-1} suggests the existence of *cis* and *trans* isomers as in the case of *ortho* phenols, where the *cis* isomers are stabilized relatively by the interaction with the *ortho* substituent. Therefore in the case of *o*-amino benzenethiol the bands at 2538 and 2600 cm.^{-1} can be assigned to the *cis* and *trans* species respectively. The value of S—H stretching frequency at 2538 cm.^{-1} which is low when compared with the S—H stretching frequency in benzenethiol at 2570 cm.^{-1} and other sulphohydril compounds indicates an intermolecular interaction between the amine and the SH group in the *cis* configuration. On the other hand the *trans* frequency at 2600 cm.^{-1} is about the same as the free S—H stretching frequency in benzenethiol at 2592 cm.^{-1} . The *cis* form being more stable these molecules would be in greater abundance than the *trans* ones.⁷ This is verified from the much greater intensity of the band corresponding to the *cis* form when compared to the other.

The distance between the nitrogen of the amino group and the hydrogen of the SH group has been calculated with the values of the bond distances and interbond angles taken from related molecules like benzene, methanethiol

and aniline. This distance comes out as 2.3 \AA , which would permit such an interaction. There is considerable evidence in literature for the formation of an intermolecular S—H...N bond where shifts of the order of 100 cm.^{-1} in the S—H frequency have been reported.⁸⁻¹⁰

Of the two C=C stretching vibrations corresponding to the modes *8a* and *8b*, only the former appears in benzenethiol at 1581 cm.^{-1} while in its *ortho* amino-derivative both of them appear as very intense Raman lines at 1581 and 1606 cm.^{-1} . In the infra-red only the latter appears as a strong band at 1610 cm.^{-1} . The intense and strongly polarised Raman line of benzene at 992 cm.^{-1} arising out of the totally symmetric oscillations appears in benzenethiol at 1000 cm.^{-1} but is completely suppressed in the Raman spectrum of *o*-amino benzenethiol. Such a suppression of this line in the spectra of hydroxy benzaldehydes has been reported earlier by Puranik and Venkata Ramiah.¹¹ The two Raman lines at 834 and 751 cm.^{-1} with a strong infra-red absorption corresponding to the latter at 746 cm.^{-1} can be assigned to the out-of-plane deformation modes *10a* and *10b*. The B_2 out-of-plane ring deformation which occurs in benzenethiol at 688 cm.^{-1} —strong both in Raman and infra-red—appears only in Raman as very weak line at 693 cm.^{-1} in *o*-amino benzenethiol. One component of the E_{2g} class (*6b*) vibration of benzene is scarcely changed in mode in the monosubstituted derivatives. However on *ortho*-substitution there is a shift towards the lower frequency depending on the nature of the substituents. This line appears at 615 cm.^{-1} in benzenethiol. Therefore a Raman line at 561 cm.^{-1} in *o*-amino benzenethiol can be assigned to this mode.

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