727. *Vibrational Frequency Correlations in Heterocyclic Molecules. Part VII.*[1] *Benzo*-1,2,3-*triazoles.*

By D. G. O'SULLIVAN.

Infrared spectra are described for a series of substituted benzo- and and 1-phenylbenzo-1,2,3-triazoles. They indicate that, in the solid state, benzotriazole possesses the cyclic diazoimino-structure and is associated by means of hydrogen bonds. Bands related to the ring systems agree with the pattern generally produced by a benzene ring fused to a five-membered ring. Between 1650 and 950 cm.$^{-1}$ little variation occurs even between benzotriazoles and their 1-phenyl derivatives, but at lower frequencies marked differences exist. Apart from those introduced by modification of the ring system, as in 1-phenylbenzotriazoles, 1-2′-quinolylbenzotriazole, and 2,3-naphthotriazole, variations depend mainly on substitution pattern.

In 5-substituted benzotriazoles a band between 896 and 811 cm.$^{-1}$ probably arises from out-of-plane vibrations of the isolated 4-hydrogen atom, and another between 888 and 803 cm.$^{-1}$ from vibrations of the adjacent 6,7-hydrogen atoms. These frequencies maintain a constant separation of 11 cm.$^{-1}$ and both are linearly dependent on the Hammett *meta* σ value for the substituent.

As many benzo-1,2,3-triazoles, particularly the nitro-compounds, have low solubilities in relevant solvents, infrared spectra were determined in the solid state in potassium bromide discs or windows. Since much criticism has been levelled at this method,[2] every determination was duplicated and, where solubilities permitted, records were obtained over suitable wavelength ranges with chloroform as solvent. In all cases good reproducibility was obtained.

Experimental.—Spectra were measured on a Perkin–Elmer 21 recording spectrophotometer fitted with a sodium chloride prism.

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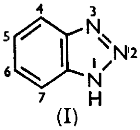
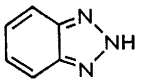
[1] Part VI, O'Sullivan, *J.*, 1960, 3278.

[2] Farmer, *Spectrochim. Acta*, 1956, **8**, 374.

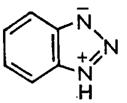
Specifically Characterised Frequencies.—Benzo-1,2,3-triazole can exist in tautomeric forms (I) and (II). Derivatives of both forms can be produced indirectly and chemical evidence favours structure (I). Molecular refraction[3] and Raman spectra[4] failed to decide between the possibilities, but the ultraviolet spectra[5] of the compound and of its 1- and 2-methyl derivative support structure (I). The following evidence arises from the infrared spectra: (i) For benzo-1,2,3-triazoles no band is present between 1680 and 1630 cm.$^{-1}$ that can definitely be referred to C=N linkages.[6] (ii) A band is present at, or slightly below, 1600 cm.$^{-1}$ (Table 1) that could arise from N=N vibrations;[7] this is also present in 1-acetyl-5-methoxybenzotriazole and in the 1-phenyl compounds (Table 1), which necessarily possess N=N bonds. (iii) Considerable similarity between the spectra of unsubstituted benzotriazoles and those substituted at position 1, particularly in the region which contains the nuclear vibrations (Table 2), suggests that the ring systems are identical in both types of structure. Consequently, the infrared data, whilst not unequivocal, also favour structure (I). The lack of chemical reactivity of benzotriazoles indicates resonance stabilisation, and structures (III) and (IV) probably make a minor contribution to the resonance hybrid. Infrared spectra do not permit decisions to be reached on the structure of benzotriazoles with substituents in positions 4 and 5.



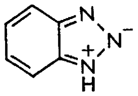
(I)



(II)



(III)



(IV)

Except for 5-bromobenzotriazole and 1-(2,4-diaminophenyl)- and 1-[2,4-di(acetamido)-phenyl]-benzotriazole no compound possesses a maximum above 3400 cm.$^{-1}$ (Table 1), showing that, generally, the NH groups are involved in hydrogen bonding. This varies between very weak bonding with 2,3-naphthotriazole to fairly strong bonding with 5-methyl- and 5-bromo-benzotriazole. The broad band between 3200 and 3100 cm.$^{-1}$ in most benzotriazoles shows that the hydrogen bonds are usually of moderate strength. This suggests that the possible resonance-stabilised association, involving structures of type (III), does not make a large contribution to the hydrogen-bonded polymer, and that, in most cases, ordinary N–H · · · N bonding is present. Stretching frequencies of the CH bonds appear as weak bands near 3000 cm.$^{-1}$ in most benzotriazoles substituted in position 1 but, being weak, they are usually obscured in the NH absorption of other compounds (Table 1).

The carbonyl stretching frequency of 1-acetyl-5-methoxybenzotriazole (Table 1) is high if compared with the *N*-acetyl carbonyl frequencies of *N*-acetylindoxyl[8] (1673 cm.$^{-1}$) and diacetylindoxyl[8] (1700 cm.$^{-1}$) and with the carbonyl frequencies of aromatic ketones.[9] This suggests that little conjugation exists with the ring system. The separation of the carbonyl frequencies in 1-[2,4-di(acetamido)phenyl]benzotriazole is surprising as the molecular environment of the two groups is similar. The frequency difference is too wide for only one carbonyl group to be involved in hydrogen bonding. Both carbonyl peaks are very sharp and the position of the NH stretching frequencies (Table 1) also shows the absence of any very strong hydrogen bonds. Either the benzotriazole ring exerts a very marked steric effect on the *o*-acetamido-group or coupling occurs between the vibrations of the two carbonyl groups in this compound.

Most of the compounds possessing an NH group give a band between 1580 and 1526

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[3] Auwers, *Ber.*, 1938, **71**, 604.

[4] Kohlrausch and Seka, *Ber.*, 1938, **71**, 1563.

[5] Specker and Gawrosch, *Ber.*, 1942, **75**, 1338.

[6] Goulden, *J.*, 1953, 997.

[7] Le Fèvre, O'Dwyer, and Werner, *Chem. and Ind.*, 1953, 378.

[8] Holt, Kellie, O'Sullivan, and Sadler, *J.*, 1958, 1217.

[9] Thompson and Torkington, *J.*, 1945, 640; Hartwell, Richards, and Thompson, *J.*, 1948, 1436; Grove and Willis, *J.*, 1951, 877; Rasmussen, Tunnicliff, and Brattain, *J. Amer. Chem. Soc.*, 1949, **71**, 1068.

TABLE 1. NH, CH, CO, C=C, N=N, *and* NO_2 *stretching and* NH *bending frequencies* 1,2,3-*triazoles.*

Subst.	ν(NH stretch)	ν(CH)	ν(CO)	ν(C=C)	ν(N=N)	ν(NH bend)	ν(ring)	ν(NO_2)
Benzotriazoles								
None	3200b			*1623*	*1600*			
5-Me	3150—2750b			1630	1594			
5-MeO	3200b			1635	1601	1526		
5-Cl	3200b			*1660* *1630*	*1595*	*1564*		
5-Br	*3440* 2750b	3025		*1623*	*1592*	*1564*	*1548*	
5-NO_2	3150b			1621	*1598*	*1565*		1525 1348
4-NO_2	3200b			1642	*1588*		1501	1532 1349
1-Ac-5-MeO			1744	1618	1601		1500	
1-*Phenylbenzotriazoles*								
None		*3100*		*1673*	1601		1509	
5-NO_2		*3100*		1616	*1600*			1528 1360
5,7-$(NO_2)_2$		*3040*		*1619*	1591			1540 1351 1501 1339
2′-NO_2		*3050*		1610	*1588*			1522 1360
2′,4′-$(NO_2)_2$		*3090*			1606		1495	1549 1356 1511
2′,4′-$(NH_2)_2$	3450—3200b			1640—1610b		1580	1525	
2′,4′-$(NHAc)_2$	3450—3200b		1693 1662	1607	1592	1537	1503	
4′,5-$(NO_2)_2$		3090 2920		1619	1597			1525 1346 1510
1-2′-Quinolyl-benzotriazole		*3140*		*1618*	1595		1506	
2,3-Naphthotri-azole	3370b	*3050* *2880*		*1636*	*1621*			

Frequencies of low intensity maxima are given in italics in this and in the following Tables. b = Broad band.

TABLE 3. *Low frequency region of* 1,2,3-*triazoles.*

Subst.	1	2	3	4	5	6	7	8	9	10	11	12	13
Benzotriazoles													
None	*900*		*878*			782 *772*	756	744					
5-Me	942	870 *850* 832	811	803			761	753				*659*	
5-MeO	*951*	*860*	835	818		809	*760*					*669*	
5-Cl	*934*		853	839		803	*760*				710	*665*	
5-Br	918		862	850		805 795	*755*				696	*668*	
5-NO_2	*945*		896	*888*	856 845 *826*	802	747	740			*698*	*669*	
4-NO_2			*882*	*870*	823	800	751	744				*669*	
1-Ac-5-MeO	958 945	858	824	818								*668*	651
1-*Phenylbenzotriazoles*													
None	*931*		*855*			791	769	754		715	700	665	
5-NO_2			904		836	803	764	751	743	731	690	669	
5,7-$(NO_2)_2$	*938* *929*					803	762	742		732	690	665	
2′-NO_2	*915*		*885*		*854*	798	768	756	748	*726*	702	*668*	*650*
2′,4′-$(NO_2)_2$	*950* 924		915	*859*	*842* 831	781	768	751	740	718		*656*	*640*
2′,4′-$(NH_2)_2$			842	834		795 785	773	750		*718*		*672*	*640*
2′,4′-$(NHAc)_2$			868	*821*		*809* 786	771	755	736		705	*668*	
4′,5-$(NO_2)_2$	*929*		862	855	839 *822*	804	763	751	740		687	*669*	
1-2′-Quinolyl-benzotriazole	*980* 942 918		879 *861*	840		789	769	750				*658*	
2,3-Naphtho-triazole	*945* *910*		873 853	824		*792*	*775*	*758*	*739*	729		*664*	*651*

TABLE 2. *Vibrational frequencies of the ring systems in* 1,2,3-*triazole derivatives.*

Subst.												
					Benzotriazoles							
None	*1464*	*1427* *1390*	*1315*		*1273*	1217	*1150*	*1120*	*1096*	*1073*	1029	1012
5-Me	1468 1442	1398 1384 1364	*1301*	*1282*	1264	1210	*1160*	1142 1136	1085	*1046*	1018	1004 990
5-MeO	1460	1431	1305		*1270*	1218	1170	1121	*1100*	1030	1021	1001
5-Cl	*1464*	*1423*	*1296*	*1282*	1262	1210	1159	1135	1111	1061	*1012*	*1005*
5-Br	*1468*	*1425* *1412*	*1288*	1278	1261	1212	*1144*	*1133*	*1104*	1051	1021	993
5-NO_2	1481 *1458*	1410	1301	1271	*1244*	1210	*1141*			1076	*1007*	989
4-NO_2	1448	1412 1390	1285		1249	1209	1152			1078 1062	*1026*	982
1-Ac-5-MeO	1444	1428 1390	1311 1291	1270	1262 1255	1212	1163	1131 1123	1090	1065	1028	958
					1-*Phenylbenzotriazoles*							
None	1468 1456	*1392*	*1299*	1285	*1251*	1195	1151	*1132*	1098	1066	1019	*949*
5-NO_2	*1482* *1465*	*1442* *1391*	*1284*			*1191*	*1178*	1139	1090	1076 1052	*1010*	*1002*
5,7-$(NO_2)_2$	*1480* *1460*	*1402*	1305			1209	*1161*		*1088*	*1058*	1003	*982*
2′-NO_2	1453		*1306*	1282	*1250*	1205 *1191*	*1151*	*1128*		1060 *1039*	*1009*	*970*
2′,4′-$(NO_2)_2$	1459	1398	1298	1271	1245	1195 *1182*	*1161*	*1141* *1128*	*1086*	1030		985
2′,4′-$(NH_2)_2$	1470	*1401* 1350	1330	1282	1252 1230	1192	1148	1138 1125	1087	1010		*966*
2′,4′-$(NHAc)_2$	*1460*	1425 1398 1374	1317	1281	1269	*1200* *1183*	*1142*	*1125*	1093	*1030*	1013	*990*
4′,5-$(NO_2)_2$	*1477*	*1446* *1407*	1318	1298	*1232*	*1206* *1193*	*1182* *1142*	*1123*	*1113*	1075	1035	1000
1-2′-Quinolylbenzotriazole	1488 1479	1450 1437 1400 1388	*1324* *1310* 1295	1289	*1243* 1214	1197	*1185* 1144	1133 *1117*	1088	1030	1015	1005 *990*
2,3-Naphthotriazole	*1460*	*1430* *1375* *1352*		1285	1223		1163		1112	1060	1010	985

The first two frequency columns contain some CH_3 bending frequencies.

cm.$^{-1}$ (Table 1), absent from other spectra, which is probably an NH deformation frequency.[10] An NO_2 stretching frequency may sometimes obscure this absorption. Strong bands, arising from the antisymmetric and symmetric NH_2 stretching vibrations,[11] are present between 1550 and 1500 cm.$^{-1}$ and between 1360 and 1339 cm.$^{-1}$, respectively, for the nitro-compounds (Table 1). Whereas all dinitro-compounds show two well-defined and very strong antisymmetric NO_2 stretching frequencies, only 5,7-dinitro-1-phenylbenzotriazole showed two low frequencies.

Vibrations of the Ring Systems above 1000 *cm.*$^{-1}$.—Pairs of characteristic bands near 1100 and 1000 cm.$^{-1}$ and near 1050 and 1000 cm.$^{-1}$ have been reported for the triazole [12] and tetrazole [13] rings respectively. Strong bands are usually found near these three frequencies with the present compounds. Occasional bands near 1440 cm.$^{-1}$ arise from deformations in methyl groups,[14] but most of the frequencies listed in Table 2 are due to vibrations of the rings and detailed assignments are not possible. The pattern of

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[10] Jones and Sandorfy, " Chemical Applications of Spectroscopy," ed. W. West, Interscience, New York, 1956, p. 520.

[11] Randle and Whiffen, *J.*, 1952, 4153.

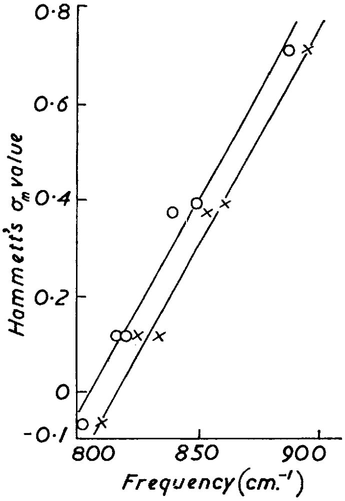
[12] Hartzel and Benson, *J. Amer. Chem. Soc.*, 1954, **76**, 667.

[13] Lieber, Levering, and Patterson, *Analyt. Chem.*, 1951, **23**, 1594.

[14] Batuev, *Zhur. fiz. Khim.*, 1949, **23**, 1399; Murti and Seshadri, *Proc. Indian Acad. Sci.*, 1938, **8**, *A*, 519.

frequencies is well maintained among the compounds, and the introduction of an additional benzene ring does not produce striking differences. Even 1-2′-quinolylbenzotriazole and 2,3-naphthotriazole preserve most of the spectral features of the simpler compounds. In the region covered by Table 2, bands related to the ring system appear near 1460, 1400, 1310, 1280, 1250, 1210, 1160, 1120, 1100, 1060, 1020, and 990 cm.$^{-1}$. These conform with the pattern of bands occurring in other compounds possessing fused benzene and 5-membered rings.[1]

Bands below 1000 *cm.*$^{-1}$.—Frequencies in column 2 of Table 3 are present only in compounds possessing methyl or methoxy-groups, and some of these bands could be C–Me and C–O–Me stretching frequencies.[15] Nitro-compounds possess bands shown in column 5, some of which might be due to C–NO_2 stretching modes.[11] Many of the remaining bands are out-of-plane CH deformation frequencies. Marked variations occur in the distribution of these frequencies; *e.g.*, compare data for benzotriazoles with those for their 1-phenyl derivatives. It is likely that the number and distribution of the frequencies are related to the pattern of substitution.[16]



Deformation vibrations probably involving isolated ring-hydrogen atoms (×) *and two adjacent ring-hydrogen atoms* (○).

Out-of-plane CH deformation modes of simple di- and tri-substituted benzenes give rise to strong bands near 850, 810, and 775 cm.$^{-1}$, derived respectively from motions involving an isolated ring-hydrogen atom, two adjacent ring-hydrogen atoms, and three adjacent ring-hydrogen atoms situated between two substituents.[17] Thus symmetrically trisubstituted benzenes possess the band near 850 cm.$^{-1}$, *para*-disubstituted benzenes possess the bands near 810 cm^{-1}, and *meta*-disubstituted benzenes exhibit the bands near 850 and 775 cm.$^{-1}$. In sets of 1,3- and 1,3,5-substituted benzenes the frequency, that arises from motions of a single ring-hydrogen, between 930 and 830 cm.$^{-1}$ is a linear function of the sum of the Hammett *meta* σ values[18] of the substituents.[19] Halogen ubstituents appear to be exceptional and behave, in this context, as if they possessed σ_m values of zero. The 1,3-substituted compounds also possess a band between 830 and 765

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[15] Herzberg, " Infrared and Raman Spectra of Polyatomic Molecules," Van Nostrand, New York, 1945, p. 353; Sheppard and Simpson, *Quart. Rev.*, 1953, **7**, 19.

[16] Lecompte, *Compt. rend.*, 1937, **204**, 1186; 1938, **206**, 1568; Whiffen and Thompson, *J.*, 1945, 268; Bell, Thompson, and Vago, *Proc. Roy. Soc.*, 1948, *A*, **192**, 498; Cole and Thompson, *Trans. Faraday Soc.*, 1950, **46**, 103; Cannon and Sutherland, *Spectrochim. Acta*, 1951, **4**, 373; McMurry and Thornton, *Analyt. Chem.*, 1952, **24**, 318; McCaulay, Lien, and Launer, *J. Amer. Chem. Soc.*, 1954, **76**, 2354; O'Sullivan and Sadler, *J. Org. Chem.*, 1957, **22**, 283.

[17] Colthup, *J. Opt. Soc. Amer.*, 1950, **40**, 397.

[18] Hammett, " Physical Organic Chemistry," McGraw-Hill, New York, 1940, p. 188; Jaffé, *Chem. Rev.*, 1953, **53**, 191.

[19] Bellamy, *J.*, 1955, 2818.

cm.$^{-1}$ arising from vibrations of three adjacent CH groups. These frequencies are also related to the sum of the σ_m values, halogen again being exceptional. For 1,4-substituted compounds,[19] a frequency between 875 and 795 cm.$^{-1}$ is linearly related to the sum of the Hammett *para* σ values in those cases in which at least one substituent formed a conjugation with the ring. The three straight lines are parallel.

Benzotriazoles, substituted at position 5, possess one isolated ring-hydrogen atom at position 4 and two adjacent ring-hydrogen atoms at positions 6 and 7. Excluding the 1-phenyl compounds, because of the CH vibrations of the phenyl group, the 5-substituted compounds possess a pair of bands between 890 and 800 cm.$^{-1}$ (Table 3) which are intense in the 5-methyl compounds (further strong absorption near 800 cm.$^{-1}$ might augment the intensities in this case), but otherwise are of moderate intensity. The higher set of frequencies ν_1 could be out-of-plane vibrations of hydrogen atoms at position 4 and the lower set ν_2 could arise from vibrations of the two adjacent hydrogen atoms. The Figure shows the relation between these sets of frequencies and the σ_m values of the 5-substituents. Regression lines for the frequencies are $\nu_1 = 817{\cdot}1 + 109{\cdot}0\sigma_m$ and $\nu_2 = 806{\cdot}3 + 109{\cdot}1\sigma_m$. Correlation coefficients are 0·990 and 0·989 respectively. Halogen substituents do not behave exceptionally. Other frequencies in the neighbourhood (Table 3) are not linearly related to either the Hammett σ_m values or the Taft σ_I values[20] of substituents. As correlation of ν_1 and ν_2 with σ_I values is poor, some resonance contribution supplements the inductive effect of substituents on the CH vibrations. The approximate proportion of this resonanc econtribution follows from the relation $\sigma_m = \sigma_I + \sigma_R/3$.[21] Tabulation of lower frequencies is greatly assisted by the existence of this correlation.

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[20] Taft, " Steric Effects in Organic Chemistry," ed. M. S. Newman, John Wiley and Sons, New York, 1956.

[21] Ref. 20, p. 594.