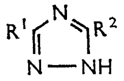
Triazoles. Part X.[1] Hydrogen Bonding and Infrared Spectra

By **E. J. Browne** * and **J. B. Polya**, Chemistry Department, University of Tasmania, Hobart, Tasmania, Australia

I.r. spectra of *N*-unsubstituted 1,2,4-triazoles in the 1700—3000 cm.$^{-1}$ region have been studied, and classified according to the intensity and number of bands characteristic of strong intermolecular hydrogen bonding. Evidence of groups showing different degrees of proton tunnelling is advanced; one of these groups appears to be involved in phosphorescent effects.

In Part IX [1] the i.r. spectra of a number of 3-pyridyl-5-aryl- and 3-pyridyl-5-acyl-1,2,4-triazoles were discussed, and broad symmetrical bands near 1900 and 2500 cm.$^{-1}$ were ascribed to proton tunnelling. Other authors have given a similar explanation for comparable observations on other classes of compounds.[2-9]

To amplify this body of information, i.r. spectra of 51 *N*-substituted and 44 *N*-unsubstituted 1,2,4-triazoles were surveyed. As expected, none of the compounds in the former group showed the bands under discussion. The *N*-unsubstituted triazoles (I) considered in this study fall broadly into two groups, to be designated series I and II. The former comprises 23 *C*-pyridyl compounds, and the latter 21 compounds with less basic substituents (alkyl, aryl, halide, and triazolyl). Rather more than one half of the compounds in each series showed bands in the 1700—2800 cm.$^{-1}$ region.



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[1] Part IX, E. J. Browne and J. B. Polya, *J. Chem. Soc.* (*C*), 1968, 824.

[2] D. Hadži, *Pure Appl. Chem.*, 1965, **11**, 435.

[3] D. Hadži, *Vestnik Slovensk. kem. Drustva*, 1958, **51**, 21.

[4] D. Hadži and N. Kobilarov, *J. Chem. Soc.* (*A*), 1966, 439.

[5] S. Detoni and D. Hadži, *Spectrochim. Acta*, 1964, **20**, 949.

[6] J. J. Braunholtz, G. E. Hall, F. G. Mann, and N. Sheppard, *J. Chem. Soc.*, 1959, 868.

[7] S. L. Johnson and K. A. Rumon, *J. Phys. Chem.*, 1965, **69**, 74.

[8] H. Zimmermann, *Ber. Bunsengesellschaft Physik. Chem.*, 1961, **65**, 821.

[9] J. Brickmann and H. Zimmermann, *Ber. Bunsengesellschaft Phys. Chem.*, 1966, **70**, 521.

TABLE 1

Series I: *C*-Pyridyl-1,2,4-triazoles (I)

No.	R^1	R^2 *	Main i.r. bands ascribable to H bonding: Maxima (cm.$^{-1}$) Band *A*	Band *C*	Intensity ratio *A*/*C* (average)	Prepn. ref.
(1)	4-Py	Bz	2473	1917	1·6	1
(2)	4-Py	p-$ClC_6H_4,\frac{1}{2}H_2O$	2480	1940	1·7	1
(3)	4-Py	*a*	2500	1910	1·7	*
(4)	3-Py	Bz	2600	1920	2·1	1
(5)	4-Py	$BzNHCH_2$	2600	1820	2·6	*
(6)	3-Py	o-$HO\cdot C_6H_4$	2670	1900 1810	2·4 3·2	1
(7)	4-Py	o-$HO\cdot C_6H_4$	2680	1900	3·0	1
(8)	4-Py	*b*	2670	1800	3·4	*
(9)	4-Py	p-$NO_2C_6H_4$	2650	1850	5·7	1
(10)	4-Py	4-Py	2650	1880	6·2	12
(11)	4-Py	H	2750	1800	7·1	13
(12)	3-Py	*c*	2750	1870	7·7	*
(13)	4-Py	Ph	2750	1770	9·6	14

[a] 3-(4-Pyridyl)-1,2,4-triazol-5-ylmethyl-, $2H_2O$. [b] 1,5-Diphenyl-1,2,4-triazol-3-yl. [c] 3-(3-Pyridyl)-1,2,4-triazol-5-ylmethyl.
* New compound.

TABLE 2

Series II: Non-pyridyl 1,2,4-triazoles (I)

No.	R^1	R^2 *	Main i.r. bands ascribable to H bonding: Maxima (cm.$^{-1}$) Band *A*	Band *C*	Intensity ratio *A*/*C* (average)	Prepn. ref.
(1)	H	H	2750	1760	2·0	
(2)	H	Cl	2750	1735	2·5	15, 16
(3)	H	*a*	2750	1720	2·5	17
(4)	H	Br	2700	1735	2·7	18
(5)	H	Me	2720	1720	3·0	19
(6)	Me	Me	2750	1750	3·5	14
(7)	Ph	Me	2730	1800	3·8	14
(8)	H	Bz	2720	1840	4·0	1
(9)	H	Ph	2750	1800	4·4	14
(10)	Me	*b*	2750	1780	5·2	*
(11)	Br	Me	2720	1740	5·8	18
(12)	Br	$HOCH_2$	2850	1700	6·4	*
(13)	Br	Br	2850	1630	6·6	18

[a] 1,2,4-Triazol-3-yl. [b] 3-Methyl-1,2,4-triazolyl-5-ylmethyl.
* New compound.

TABLE 3

3-5-Disubstituted-1,2,4-triazoles (I) [1,14,20]

R^1	R^2 *	M.p.	Yield (%)	Found (%) C	H	N	Formula	Required (%) C	H	N
3-Py	*a*	297—298°	50	58·7	4·0	36·4	$C_{15}H_{12}N_8$	59·2	4·0	36·85
2-Py	*b*	235—236 [f]	43	61·2	4·8	33·75	$C_{17}H_{16}N_8$	61·4	4·85	33·75
2-Py	$HOCH_2$	230—231 [g]	58	54·1	4·65	31·3	$C_8H_8N_4O$	54·55	4·6	31·8
3-Py	*c*	316—318 [h]	19	59·05	4·3		$C_{15}H_{12}N_8$	59·2	4·0	
4-Py	*d*	319—320 [h]	31	53·2	4·65	32·45	$C_{15}H_{12}N_8,2H_2O$	52·9	4·75	32·95
4-Py	$BzNHCH_2$	211—212 [i]	65	64·25	4·9	25·0	$C_{15}H_{13}N_5O$	64·5	4·7	25·1
4-Py	*e*	318—319 [j]	51	68·8	4·1	26·5	$C_{21}H_{15}N_7$	69·0	4·15	26·8
4-Py	$HOCH_2$	241—243 [g]	63	55·0	4·7	31·15	$C_8H_8N_4O$	54·55	4·6	31·8
Me	*a*	268—269 [i]	32	47·2	5·6		$C_7H_{10}N_6$	47·2	5·65	47·2
Br	$HOCH_2$	118—119 [k]	7	20·2	2·4		$C_3H_4N_3BrO$	20·25	2·25	
					Br, 44·3				Br, 44·9	

[a] 3-Methyl-1,2,4-triazol-5-ylmethyl. [b] 3-(2-Pyridyl)-1,2,4-triazol-5-ylethyl. [c] 3-(3-Pyridyl)-1,2,4-triazol-5-ylmethyl. [d] 3-(4-Pyridyl)-1,2,4-triazol-5-ylmethyl, $2H_2O$. [e] 1,5-Diphenyl-1,2,4-triazol-3-yl. Recryst. from: [f] EtOH. [g] H_2O. [h] PyH. [i] EtOH–Et_2O. [j] PyH–Et_2O. [k] Et_2O–light petroleum.

These two series do not exhaust all possibilities. Thus preliminary observations on triazolones, triazolthiones, aminotriazoles, and salts of triazoles suggest that other examples of such bands will be found, especially in the last mentioned group.

Strong absorption in the 2400—3200 cm.$^{-1}$ region is characteristic of *N*-unsubstituted triazoles,[10,11] but the number and relative intensities of bands in this region display significant differences.

Members of the two series showing more than one of the critical bands are listed in Tables 1 and 2. The characteristics of new compounds are summarised in Table 3.

From a survey of compounds known to show the asymmetric type of proton tunnelling one might deduce that the simultaneous presence of both acid and base centres is necessary.[4,7,21,22]

In series I the effect is usually most pronounced with 4-pyridyl, less so with 3-pyridyl, and fails in the case of 2-pyridyl substituents. Probably steric effects are involved since we have noted that all the isomeric pyridylacrylic acids [23] display the bands in question; the characteristic criteria decrease in the order 4- > 2- > 3-. In series I the molecules are relatively large, and substituents that make for close, coplanar packing assist the effect. Carbonyl, hydroxyphenyl, and triazolyl are examples, provided that they are in positions that make intramolecular bonding possible. Inductive effects may be shown by comparison of substituents [Table 1, see especially (9), (10), (11), and 13)].

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[10] H. G. O. Becker, H. J. Moll, and H. Haufe, *Wiss. Z. tech. Hochschule Chem. Leuna-Merseburg*, 1966, **8**, 120.

[11] W. Otting, *Ber.*, 1956, **89**, 2887.

[12] U. P. Basu and S. Dutta, *J. Org. Chem.*, 1964, **30**, 3562.

[13] D. H. Jones, R. Slack, S. Squires, and K. R. H. Wooldridge, *J. Medicin. Chem.*, 1965, **8**, 676.

[14] I. Ya. Postovskii and N. N. Vereschchagina, *Zhur. obschei Khim.*, 1959, **29**, 2139.

[15] R. Miethchen and C. F. Kröger, *Z. Chem.*, 1967, **7**, 184.

[16] J. Thiele and W. Manchot, *Annalen*, 1898, **303**, 33.

[17] E. L. Rinman, *Ber.*, 1897, **30**, 1193.

[18] C. F. Kröger and R. Miethchen, *Ber.*, 1967, **100**, 2250.

[19] H. Paul, G. Hilgetag, and G. Jähnchen, *Ber.*, 1968, **101**, 2033.

[20] E. J. Browne and J. B. Polya, *J. Chem. Soc.*, 1962, 5149.

[21] D. Hadži, *J. Chem. Soc.* (*A*), 1967, 48.

[22] D. Hadži, C. Klofutar, and S. Oblak, *J. Chem. Soc.* (*A*), 1968, 905.

[23] C. S. Marvel, L. E. Coleman, jun., and G. P. Scott, *J. Org. Chem.*, 1955, **20**, 1785.

Similar influences seen in the series of the triazoles without pyridyl substituents are less marked. Functional groups that increase the strength of acidic centres may simultaneously weaken the basic centres.

The phenomena ascribed to proton tunnelling in unsymmetrical cases refer to intermolecular bridges. The distinction from intramolecular effects can be made on the usual criteria of spectra of solutions, provided solubilities are sufficient. Hence we had difficulties with the high melting and relatively insoluble members of series I; the same compounds were difficult to deuteriate. Accepting Hadži's nomenclature [2,4] we shall call the upper band *A* and the lower band *C*. An intermediate band, *B*, sometimes observed, did not appear in series I or II. A third band previously reported [1] [(Table 1, (6)] is best regarded as a split *C* band.

Several authors [2-4,7,8] have observed that on deuteriation band *A* shifts to *ca.* 2100 cm.$^{-1}$ and band *C* disappears; no generally accepted explanation exists. In our experience, compounds that undergo at least partial deuteriation show this spectroscopic effect in a consistent way.

According to Hadži [2,4] the strength of the hydrogen bridge is inversely correlated with the wave number of band *A* and also with the ratio of the intensities *A*/*C*. These relationships are illustrated in Figures 1 and 2, referring to series I and II respectively. With broad, overlapping bands intensity determinations can be only approximate.[2] Most relevant bands, notably in the first members of series I, were smooth and symmetrical; others showed small superimposed peaks. The greatest irregularity, which was not extreme, was seen in band *C* of series II. Band overlap was variable, but estimates of band width showed resemblances within each group [*viz.* band *A*: series I, 1050—1250 cm.$^{-1}$; series II, 1150—1350 cm.$^{-1}$: band *C*: series I and II, 300—420 cm.$^{-1}$]. For comparison of overlapping bands of similar shape and width the use of graphical integration did not seem to offer greater accuracy than measurement of peak heights which were, therefore, used for intensity estimations.

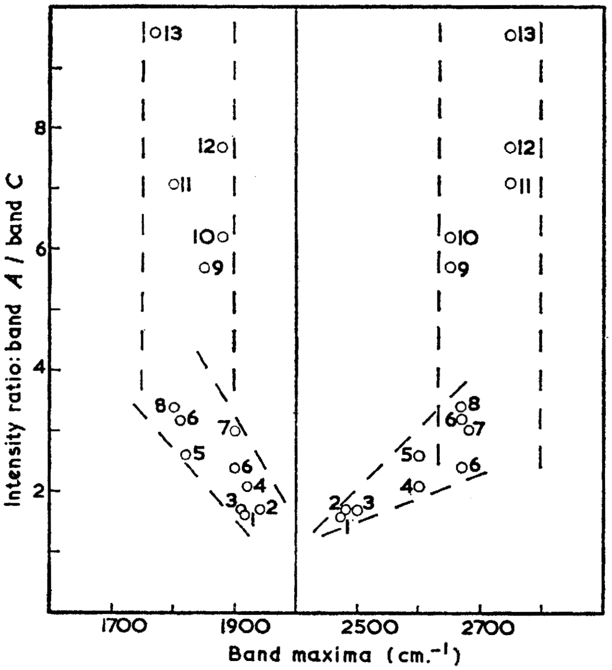

FIGURE 1 Series I: *N*-unsubstituted pyridyl-1,2,4-triazoles

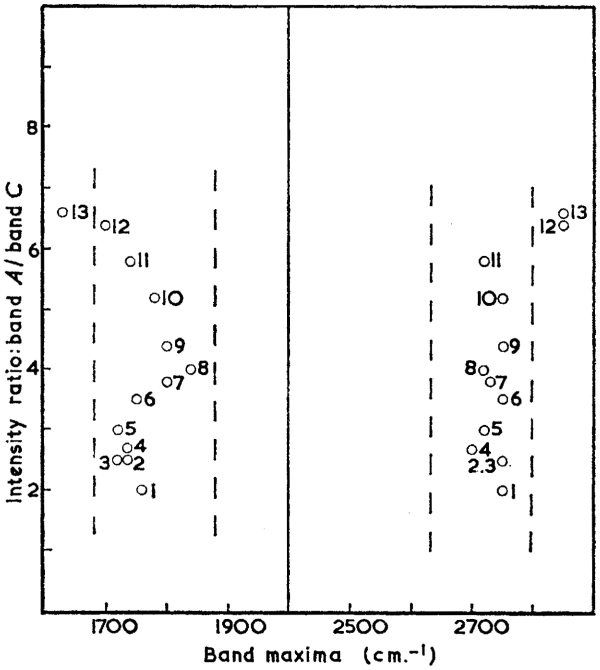

FIGURE 2 Series II: *N*-unsubstituted non-pyridyl-1,2,4-triazoles

Band *A* positions for series I are, on the whole, lower than for series II, as may be expected considering that the pyridyls in the former provide more basic centres than present in the latter. In series I the first members obey Hadži's rule, and the others are effectively invariant. The suggestion of two families in this series is borne out by the general aspects of the spectra; there may also be some direct relationship between the position of band *C* and the bond strength, at least for the first members.

In series II only the invariant family has been observed, and this appears to be the same as the corresponding family in series I. In the last members [(12) and (13)] the effect is barely observable. This raises the question whether members of the invariant families are to be regarded as exhibiting proton tunnelling at all. *N*-Unsubstituted 1,2,4-triazoles that are clearly negative in this respect either lack bands ascribable to hydrogen bonding [1] or show only one, resembling an intense *A* band, usually above 2800 cm.$^{-1}$. In the previous communication [1] only the strong *A* band was reported for some compounds now included in the invariant family.

Of the related parent azoles, proton tunnelling has been well established in the case of imidazole [8,9,24]; 1,2,4-triazole and tetrazole show close spectral similarities.[11] N.m.r. data and their analysis [25-30] also reveal the expected similarities, which have been interpreted as evidence for proton tunnelling.[25] Our own measurements agree with the literature data for CH values, and provide additional information in respect of NH values (Table 4).[25,28]

TABLE 4

Chemical shifts of molten azoles

	Temp.	N–H Signal *
1,2,4-Triazole	125°	11·40
	137	11·34
3-Methyl-1,2,4-triazole	110	11·13
3,5-Dimethyl-1,2,4-triazole	148	10·88
Imidazole	95	10·68
	110	10·52
Pyrazole	70	10·22
	90	9·98

* In p.p.m. downfield from the main peak of dimethyl sulphoxide, as external standard.

X-Ray crystallography [31-35] suggests that 1,2,4-triazole is more closely related to imidazole and purine than to pyrazole; but in solution, up to concentrations of 2M, 1,2,4-triazole more closely resembles pyrazole than imidazole.[25] In view of this ' duality ' of 1,2,4-triazole, it is necessary to stress that our studies were concerned with solids only.

Some commercial preparations of 1,2,4-triazole show intense, long-lived (12—14 sec.) green phosphorescence at room temperature. Sublimation *in vacuo* of these samples produces non-phosphorescent material. The phosphorescence can be restored by heating this sublimed triazole above its melting point, by electrolysis of the melt, or by exposure to *X*-rays or even to sunshine. Hence the effect is not due to the trace metals present in the original samples, nor to triazole itself. The residue (II) (*ca.* 1 part in 2000), although not phosphorescent by itself, produces the full effect in any 1,2,4-triazole with which it is fused, or in a frozen ethanolic solution.

By heating triazole prepared by sublimation from phosphorescent material the same substance (II) is re-formed, on the evidence of phosphorescence spectra (incident maximum 345 mμ, and peak maximum 490 mμ). The fluorescence spectrum (incident maximum 365 mμ and peak maximum 415 mμ) also shows identity. The u.v. spectrum shows a strong, broad *K* band with a flat maximum near 223 mμ.

Clearly the presence of a non-phosphorescent substance (III), co-subliming with the 1,2,4-triazole and acting as a precursor or initiator for (II), may be assumed.

Both i.r. and mass spectra of the residue (II) indicate the presence of 1,2,4-triazole and 4-amino-1,2,4-triazole as major components. The next strongest parent-peak in the mass spectrum (*ca.* 2% of the base peak) was at 136, suggesting a bitriazole. This was not inconsistent with i.r. spectroscopic evidence, but the two known bitriazoles (3,3′ ref. 17 and 3,4′ ref. 36) are not responsible for the effect by themselves.

We have synthesised phosphorescent 1,2,4-triazole by Pellizzari-type reactions under near-neutral conditions.[37] The scarlet colour observed on oxidation of triazole containing (III) suggests that the latter may be a dihydrotetrazine (*cf.* refs. 37 and 38) stabilised in association with triazole.

Although 1,2,4-triazole is not primarily responsible for the effect, it constitutes an exceptionally favourable environment. Fusion of the active residue (II) with a wide variety of 1,2,4-triazoles produces a similar, but less intense and shorter-lived (1—7 sec.) phosphorescence in some members of series II, parallel with the order assigned on proton-tunnelling criteria. Phosphorescence (6—7 sec.) is also observed on fusion of (II) with tetrazole, but not with imidazole or pyrazole.

1,2,4-Triazoles with phenyl or pyridyl substituents, and those showing no significant evidence of proton tunnelling, did not produce phosphorescence under these conditions.

EXPERIMENTAL

I.r. spectra were determined as Nujol mulls on a Perkin-Elmer spectrophotometer, Model No. 221. ^{1}H N.m.r. spectra were recorded with a JEOL JNM-4H-100 spectrometer.

Phosphorescent 1,2,4-*Triazole*.—(*a*) Formamide (9 g.), formhydrazide (12 g.), diformhydrazide (4·4 g.), and hydrazine dihydrochloride (10·5 g.), were heated on a steam-bath for 1 hr. The mixture was distilled, and the product collected at 260—265° (9 g.). Recrystallisation from ethyl acetate gave 1,2,4-triazole (m.p. 119—121°; period of phosphorescence 6—7 sec.).

(*b*) Hydrazine dihydrochloride (15·8 g.), sodium carbonate (8 g.), ammonium formate (13 g.), and diformhydrazide (2·2 g.), heated on a steam-bath for 30 min., and then distilled, gave 1,2,4-triazole (1·1 g.; period of phosphorescence 5—6 sec.).

1,2,4-Triazole prepared by method (*a*) was sublimed *in vacuo* to give non-phosphorescent material. When heated at 140—160° for 3 hr. this regenerated the phosphorescence (8—9 sec.).

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[24] Marcia Cordes de N. D. and J. L. Walter, *Spectrochim. Acta*, 1968, **24**, *A*, 237.

[25] N. Joop and H. Zimmermann, *Ber. Bunsengesellschaft Phys. Chem.*, 1962, **66**, 440, 541.

[26] A. Mannschreck, W. Seitz, and H. A. Staab, *Ber. Bunsengestellschaft. Phys. Chem.*, 1963, **67**, 470.

[27] W. Freiberg and C. F. Kröger, and R. Radeglia, *Tetrahedron Letters*, 1967, 2109.

[28] L. T. Creagh and P. Truitt, *J. Org. Chem.*, 1968, **33**, 2956.

[29] G. B. Barlin and T. J. Batterham, *J. Chem. Soc.* (*B*), 1967, 516.

[30] R. Jacquier, M. L. Roumestant, and P. Viallefont, *Bull. Soc. chim. France*, 1967, 2630.

[31] H. Deuschl, *Ber. Bunsengesellschaft Phys. Chem.*, 1965, **69**, 550.

[32] S. Martinez-Carrera, *Acta Cryst.*, 1966, **20**, 783.

[33] H. W. W. Ehrlich, *Acta Cryst.*, 1965, **13**, 946.

[34] D. G. Watson, R. M. Sweet, and R. E. Marsh, *Acta Cryst.*, 1965, **19**, 573.

[35] B. Pullman, H. Berthod, and J. Caillet, *Theoret. Chim. Acta*, 1968, **10**, 43.

[36] R. H. Wiley and A. J. Hart, *J. Org. Chem.*, 1953, **18**, 1368.

[37] G. Pellizzari, *Gazzetta*, 1894, **24**, 222.

[38] G. Pellizzari, *Gazzetta*, 1909, **39**, 520.

The first nine compounds reported in Table 3 were prepared by condensation of acylhydrazides and imidoates, and thermal cyclisation of the intermediate amidrazones.[1 14,20] 3-*Bromo*-5-*hydroxymethyl*-1,2,4-*triazole* was prepared from the corresponding 3-amino-compound (cf. ref. 16).

We acknowledge the assistance of the C.S.I.R.O., Division of Applied Chemistry, Melbourne, for the determination of the mass spectrum; and of Mr. J. L. Laver for the determination of the fluorescence and phosphorescence spectra.

[8/1625 *Received, November* 12*th*, 1968]