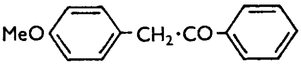
306. *Interaction at a Distance in Conjugated Systems. Part III.*[1] *Effect of Aryl and Heteroaryl Groups on the Infrared Intensities of* C=C *and* C≡C *Stretching Bands.*

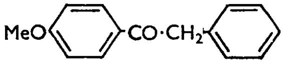
By A. R. KATRITZKY, A. J. BOULTON, and D. J. SHORT.

The intensities of the C=C and C≡C stretching modes in 4-substituted stilbenes and tolans depend on the magnitude of the conjugative power of the substituent, but not on whether it is an electron-donor or -acceptor. The 2- and 4-pyridyl and the 2- and 4-(pyridyl 1-oxide) groups behave as strong electron-acceptors; electron-withdrawing substituents in the phenyl ring in styryl- and phenylethynyl-pyridine 1-oxide are unable to cause the *N*-oxide group to donate electrons.

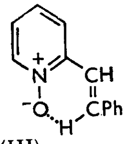
THE intensity of an infrared absorption band is determined by the rate of change of dipole moment with the normal co-ordinate at the equilibrium position. For vibrations which are effectively localised in one bond, such as the C=C and C≡C stretching frequencies, and within a series of closely related molecules, it is a reasonable assumption that this will depend on the magnitude of the charge asymmetry in that bond (cf. discussion in ref. 2). The intensities of these bands in a series of diaryl-acetylenes and -ethylenes should therefore afford information about the net displacement of electrons from one ring towards the other in these compounds.



(I)



(II)



(III)

We wished to investigate electronic interactions in styryl- and phenylethynyl-pyridines and -pyridine 1-oxides by this method. For comparison, a series of substituted stilbenes and tolans was prepared. 4-Methoxytolan had been reported by Orékhoff and Tiffeneau [3] to result from 4-methoxystilbene dibromide and aqueous potassium carbonate. In our hands this procedure gave a product of m. p. 89—91° not raised by further recrystallisation and in agreement with that reported by those authors (89—90°), but the compound showed a carbonyl band in the infrared spectrum, and analysis gave $C_{15}H_{14}O_2$. The methoxytolan had obviously been hydrated to compound (I) or (II); these compounds are both known and have m. p.s of 94° [4] or 98° [5] (I) and 76° [6] or 77—78° [7] (II). The infrared spectrum supported (I) but did not exclude a mixture with a small amount of (II). (i) The position of the ν C=O at 1677 cm.$^{-1}$ was close to that of acetophenone [8] at 1680 cm.$^{-1}$ as expected for (I), whereas that for (II) should be somewhat lower. (ii) The intensities of the bands at 1611 cm.$^{-1}$ (105) and at 1514 cm.$^{-1}$ (390) are those expected for (I); these bands should be of respectively higher and lower intensity in (II).[9] (iii) The position of the MeO–Ar stretching frequency at 1248 cm.$^{-1}$ also supports (I).[10]

The infrared spectra of the above stilbenes and tolans, and of related stilbazoles, phenylethynylpyridines, and their *N*-oxides were determined as 0·189M-solutions in

[1] Part II, preceding paper.

[2] Katritzky, *J.*, 1958, 4162.

[3] Orékhoff and Tiffeneau, *Bull. Soc. chim. France*, 1925, **37**, 1416.

[4] Buck and Ide, *J. Amer. Chem. Soc.*, 1932, **54**, 3013.

[5] Barnes, Cooper, Tulane, and Delaney, *J. Org. Chem.*, 1943, **8**, 153.

[6] Ney, *Ber.*, 1888, **21**, 2450.

[7] Meisenheimer and Jochelson, *Annalen*, 1907, **355**, 291.

[8] Katritzky, Monro, Beard, Dearnaley, and Earl, *J.*, 1958, 2182.

[9] Katritzky and Simmons, *J.*, 1959, 2051.

[10] Katritzky and Coats, *J.*, 1959, 2062.

TABLE 1.

			1		2		3		4		5		6		7		8	
			Disubstituted *trans*-ethylene										Disubstituted acetylene					
			$\nu C{=}C$		?		CH=CH γCH		?		?		$C{\equiv}C$		?		Ph	
No.	First substit.	Second substit.	cm.$^{-1}$	ε_A	cm.$^{-1}$	ε_A	cm.$^{-1}$	ε_A	cm.$^{-1}$	ε_A	cm.$^{-1}$	ε_A	cm.$^{-1}$	ε_A	cm.$^{-1}$	ε_A	cm.$^{-1}$	ε_A
1	Ph	$C_6H_4{\cdot}NMe_2$-*p*	1630 *	40	980 *	15	959	170	(—)		847	15	NA		NA		NA	
2	Ph	$C_6H_4{\cdot}OMe$-*p*	1637	10	979 *	10	959	170	927 *	10	852	35	2220	20	1138	40	911	15
3	Ph	C_6H_4Me-*p*	1638	5	981 *	15	962	180	942 *	15	855	15	2226[a]	7	—		911	20
4	Ph	Ph	—		982	25	960	180	—		—		—		—		914	25
5	Ph	C_6H_4Cl-*p*	1630	5	982 *	15	962	175	941	20	857	30	2226[a]	4	1138	10	913	25
6	Ph	$C_6H_4{\cdot}NO_2$-*p*	1636	40	982	10	966	130	954	120	850 ‡	95	2221	80	1136	5	915	20
7	2-Py	Ph	1644	35	986 *	40	967	100	952	85	858	10	2220	30	(—)		915	10
8	3-Py	Ph	1639	15	978	15	962	140	942 *	15	—		NA		NA		NA	
9	4-Py	$C_6H_4{\cdot}NMe_2$-*p*	1633	90	—		964	150	(—)		($CHCl_3$)		NA		NA		NA	
10	4-Py	$C_6H_4{\cdot}OMe$-*p*	1639	40	—		966	125	953 *	30	876	20	2220	90	1142	65	—	
11	4-Py	C_6H_4Me-*p*	1635	40	(—)		968	155	953	30	875	15	2230	70	—		—	
12	4-Py	Ph	1638	25	985 *	25	967	145	955	50	867	20	2225	40	—		915	10
13	4-Py	C_6H_4Cl-*p*	1639	25	—		966	155	955	40	873	25	2225	40	—		—	
14	4-Py	$C_6H_4{\cdot}NO_2$-*p*	1630	10	(—)		969	135	952	85	876	15	2225	5	—		—	
15	2-PyO	Ph	1632	70	986 *	25	964	100	—		861 *	25	NA		NA		NA	
16	4-PyO	$C_6H_4{\cdot}NMe_2$-*p*	(—)		—		958	130	(—)		857	40	NA		NA		NA	
17	4-PyO	$C_6H_4{\cdot}OMe$-*p*	1634	50	—		959	140	—		860 *	30	NA		NA		NA	
18	4-PyO	C_6H_4Me-*p*	1638	60	—		963	155	943	15	865	35	2220	70	1141	50	—	
19	4-PyO	Ph	1633	30	985	10	961	155	—		860 †	70	2225	40	1145	80	915	10
20	4-PyO	C_6H_4Cl-*p*	1631	50	—		961	170	941	20	865	25	2225	15	1140	115	—	
21	4-PyO	$C_6H_4{\cdot}NO_2$-*p*	1636 *	10	—		964	120	953	105	($CHCl_3$)		2225	5	1143	135	—	

* Shoulder. † Band considered to be the superimposition of two peaks. — Absence of band. (—) Band masked by stronger absorption. ($CHCl_3$) Band masked by solvent. ‡ Intensity gained by strong overlap. [a] Measurements made on solutions >0·2M.

TABLE 2. *Nuclear bands for stilbenes and tolans.*

		1		2		3		4		5		6		7		8		9		10		11		12		13	
		Mono + *p*-di		Mono + *p*-di		*p*-Di		Mono		Mono		*p*-Di		*p*-Di		*p*-Di		*p*-Di		Mono		Mono		*p*-Di		*p*-Di	
		A, νCC		B, νCC		A, νCC		A, νCC		B, νCC		B, νCC		βCH		βCH		βCH		βCH		βCH		βCH		γCH	
No.	Subst.	cm.$^{-1}$	ε_A	cm.$^{-1}$	ε_A	cm.$^{-1}$	ε_A	cm.$^{-1}$	ε_A	cm.$^{-1}$	ε_A	cm.$^{-1}$	ε_A	cm.$^{-1}$	ε_A	cm.$^{-1}$	ε_A	cm.$^{-1}$	ε_A	cm.$^{-1}$	ε_A	cm.$^{-1}$	ε_A	cm.$^{-1}$	ε_A	cm.$^{-2}$	ε_A
Compounds *p*-$X{\cdot}C_6H_4{\cdot}CH{=}CH{\cdot}Ph$																											
1	NMe_2	1608 1595	400 310	1555*	40	1522	340	1484	90	(—)		1415	25	1270	15	1165	180	(—)		1072*	25	1028	15	1005	15	809	180
2	OMe	1607 1597	180 150	1577	45	1513	410	(—)		1451‡	60	1421	25	1267*	170	1175	260	1109	25	1071	20	(—)		(—)		816	150
3	Me	1599	45	1580	5	1514	90	1497	40	1453	50	1419	10	1266	5	1183	10	1108	10	1073	15	1028	20	1019	10	802	120
4	Cl	1598	20	1580*	10	1499	170	1472	15	1454	40	1409	25	—		—		1115	25	1073	15	1028	15	1012	85	811	170
5	NO_2	1599	260	(—)		(—)		(—)		1454	45	—		1261	5	1195 1184	25 45	1111	180	1074	15	1030	10	1010	5	829	80
Compounds *p*-$X{\cdot}C_6H_4{\cdot}C{\equiv}C{\cdot}Ph$																											
6	OMe	1606 1596	170 190	1573	50	1512	460	1492*	25	1444†	85	1416	10	1312*	35	1174	190	1106	35	1069	15	(—)		(—)		831	260
7	Me	1598	60	1575	10	1512	190	1489	40	1445	45	1407	5	1307	10	1180	10	1103	15	1068	20	1025	15	1019	20	815	200
8	Cl	1602* 1599	20 40	1575	10	1497	360	1484*	65	1445	45	1400	40	1310	10	—		(—)		1069	25	1025	10	1014	155	827	340
9	NO_2	1598	280	—		1500	130	(—)		1445	35	1405	10	1286	60	1176	35	1108	150	1070	15	1026	15	1014	15	854 830	260 60

purified chloroform in a 0·106 mm. cell. As in previous work, apparent extinction coefficients were recorded; the justification for this and the errors and approximations involved therein have been discussed,[8] as has the degree of reproducibility that may be expected on other machines.[11] The bands connected with the –CH=CH– and –C≡C– groups are collected in Table 1.

The intensities of the C=C and C≡C stretching bands in the stilbenes and tolans (Table 1, Nos. 1—6) depend as expected on the conjugative power of the substituent, but not on whether the substituent is an electron-donor or -acceptor. The intensity of the C=C stretching band in the unsubstituted stilbazoles and their 1-oxides (Nos. 7, 8, 12, 15, 19) is (30—40) * for the 2-Py, 4-Py, and 4-PyO compounds, *i.e.*, comparable with that of 4-nitrostilbene. The 3-Py compound has a lower intensity (15); the 3-position of the pyridine ring is known to accept electrons less readily than the 2- or the 4-position. The 2-PyO compound has a higher intensity (70); this may be due to its strong electron-attracting power [12] or to a special interaction (as III). In the unsubstituted phenylethynylpyridines the available 2-Py, 4-Py, and 4-PyO compounds all have intensities in the range (30—40), about half that of 4-nitrotolan.

When the series 4-Py·CH:CH·C_6H_4X and 4-Py·C:C·C_6H_4·X are considered (Table 1, Nos. 9—14), the intensities drop smoothly as X changes from the strongly electron-donating NMe_2 group to the electron-accepting NO_2 group. The intensities of all the 4-PyO compounds are similar to those of their 4-Py analogues, indicating that the 4-substituted pyridine oxide ring is acting as an electron-acceptor throughout, and that in 4-PyO·CH:CH·C_6H_4·NO_2 and 4-PyO·C:C·C_6H_4·NO_2 the nitro-group is unable to polarise the $N^+–O^-$ group so as to cause it to donate electrons. This is in agreement with our results in the phenylpyridine 1-oxide series.[13] †

The positions of the C=C and C≡C stretching bands are 1644—1630 [1635 ± 4] and 2230—2220 cm.$^{-1}$, in good agreement with previous work.[14a, 15a]

The CH=CH *Out-of-plane* CH *Deformation.*—In contrast to the stretching mode, this mode (Table 1, col. 3) is of essentially constant intensity as well as position, 969—959 cm.$^{-1}$ (125—180) [963 ± 3 cm.$^{-1}$ (150 ± 20)], except that in the 2-substituted compounds (Nos. 7, 15) the ε_A is lower (100), which may be due to interactions of type (III). This band was found at [980 ± 2 cm.$^{-1}$ (130 ± 25)] for a series of β-aryl and β-heteroaryl acrylates (X·CH:CH·CO_2Et) [8] and occurs at 968—964 cm.$^{-1}$ (90—110) in *trans*-dialkylethylenes.[14b] A careful study of the intensity of this band for stilbenes (in CS_2, 3 mm. cells) has been made by Orr,[16] who found that the intensity area was relatively constant but that the band width was increased, and the peak height decreased, by *ortho*-substituents. Orr found peak intensities of *ca.* 340 for unhindered compounds; the discrepancy with the present values is presumably because Orr's values were corrected (by up to 25%) from the ε_A values observed because the solutions used by him were much more dilute than in the present work, and because of the difference in solvents.

Stilbenes and stilbazoles with a monosubstituted benzene ring attached to the ethylenic bond show a band or pronounced shoulder at *ca.* 985—980 cm.$^{-1}$ (col. 2). A band or

---

* Throughout this paper Py = pyridine, PyO = pyridine 1-oxide, and preceding numerals indicate the position of substitution. Parentheses enclose apparent extinction coefficients and square brackets enclose arithmetic means and standard deviations.

† The fact that the intensity variations for the olefins parallel those for the acetylenes indicates that possible coupling in the former class of compound between the C=C and the benzene vibration near 1600 cm.$^{-1}$ is not important to the argument.

[11] Katritzky and Lagowski, *J.*, 1958, 4155.

[12] Katritzky, *Quart. Rev.*, 1952, **10**, 395.

[13] Katritzky and Simmons, *J.*, 1960, 1511.

[14] R. N. Jones and Sandorfy, in Weissberger, "Technique of Organic Chemistry, Vol. IX. "Chemical Applications of Spectroscopy," Interscience Publ., Inc., London, 1956: (*a*) pp. 369, 385; (*b*) p. 379; (*c*) p. 382.

[15] Bellamy, "Infrared Spectra of Complex Molecules," 2nd edn., London, Methuen, 1958, (*a*) pp. 35, 59; (*b*) p. 52.

[16] Orr, *Spectrochim. Acta*, 1956, **8**, 218.

shoulder at 955—940 cm.$^{-1}$ occurs in stilbenes and stilbazoles with a pyridyl or nitrophenyl group and in some other compounds (col. 4).

The stilbenes and stilbazoles show a band (absent in Nos. 4, 8) at 876—847 cm.$^{-1}$ (10—40) [862 ± 9 cm.$^{-1}$ (25 ± 10)], which is presumably a skeletal mode; Brown and Sheppard[17] have shown that the –CH=CH– out-of-plane out-of-phase mode (the mode usually referred to merely as " out-of-plane " is the in-phase one) absorbs near 750 cm.$^{-1}$. The –CH=CH– in-plane modes occur near 1300 cm.$^{-1}$,[14c,15b] but are of low intensity: the stilbenes and the stilbazoles show one or two bands or shoulders in this region at *ca.* 1320 and 1305 cm.$^{-1}$ (5—10). Bands at 1304 cm.$^{-1}$ (65) and 1304 cm.$^{-1}$ (100) in Nos. 10 and 17 respectively are probably connected to the OMe groups.[10]

The tolans and phenylethynyl-pyridines containing a phenyl group show a band (col. 8) at 915—911 cm.$^{-1}$ (10—25) [913 ± 2 cm.$^{-1}$ (15 ± 5)] which is probably a nuclear vibration.[11] A band of unknown origin is shown (col. 7) at 1145—1136 cm.$^{-1}$ in the pyridine oxides and several other compounds.

Bands due to Ring Vibrations.—With few exceptions, all the remaining bands of $\varepsilon_A \geqslant 15$ could be assigned to ring or substituent vibrations. Table 2 gives the bands assigned to the mono- and *para*-di-substituted benzene rings of the stilbenes and tolans. Bands due to the monosubstituted rings are relatively invariant, demonstrating the small effect of remote substitution. Substituents directly attached to the disubstituted rings affect the bands in a manner in agreement with the conclusions previously reached.[2]

Bands arising from the mono- and *para*-di-substituted benzene rings[9] in the heterocyclic compounds have already been published, as have those of the 2- and 3-substituted heterocyclic rings.[18]

TABLE 3. *Nuclear bands.*

4-Substituted pyridines

Position (cm.$^{-1}$) Range	Position (cm.$^{-1}$) Mean	Intensity (ε_A) Range	Intensity (ε_A) Mean
1603—1591	1598	220—390	300
1553—1550	1552 [a] [b] absent or masked	15—20	15
(band near 1500 cm.$^{-1}$ masked)			
1419—1415 [a] 1410—1407 [b]	1417 1409	40—70	50
1068—1064	1066	5—15	10
994—990	992	35—75 [c]	55
[a] (below 805 cm.$^{-1}$) 820—818 [b]	819	120—160	140

4-Substituted pyridine 1-oxides

Position (cm.$^{-1}$) Range	Position (cm.$^{-1}$) Mean	Intensity (ε_A) Range	Intensity (ε_A) Mean
(band near 1600 cm.$^{-1}$ masked)			
1495—1475	1485	195—420	295
1451—1441	1446	25—60	50
1259—1243 [a] 1264—1260 [b]	1249 1261	290—460	370
1172—1165	1169	260—390 [a] 150—280 [b]	330 220
1095—1093	1094	15—30	20
1033—1028	1031	95—120	110
852—840	846	40—75 [ad] 220—310 [b]	50 270
833—820	828	130—310	200

a refers to stilbazoles, *b* to phenylethynylpyridines (where no designation is given the two classes are considered together), *c* except the NMe_2 compound which showed ε_A 120, *d* except the Cl compound which showed ε_A 140.

Nuclear bands for the 4-pyridyl compounds (Table 1, Nos. 9—14) and the 4-substituted pyridine 1-oxides (Table 1, Nos. 16—21) are summarised in Table 3. These bands have already been discussed, and the present results agree with the conclusions reached.[18a,c]

EXPERIMENTAL

Stilbenes.—The following 4-substituted stilbenes were prepared by the methods indicated: dimethylamino-[19] (25%), m. p. 150°, sublimed at 145°/0·1 mm. (lit.,[19] m. p. 150°); methoxy-[20] (20%), needles, m. p. 140—141·5°, sublimed at 130°/0·1 mm. (Found: C, 85·8; H, 6·7. Calc. for $C_{15}H_{14}O$: C, 85·8; H, 6·7%) (lit.,[20] m. p. 136°); methyl-[21] (45%), m. p. 119° (lit.,[21] m. p.

---

[17] Brown and Sheppard, *Trans. Faraday Soc.*, 1955, **51**, 1611.
[18] Katritzky and co-workers, *J.*, 1958, (*a*) 2192, (*b*) 2195, (*c*) 2198, (*d*) 2202, (*e*) 3165.
[19] Dey and Row, *J. Ind. Chem. Soc.*, 1925, **1**, 285; *Chem. Zentr.*, 1925, II, 1763.
[20] Hewitt, Lewcock, and Pope, *J.*, 1912, **101**, 606.
[21] Drefahl and Plötner, *Chem. Ber.*, 1958, **91**, 1276, 1280.

119°); chloro-[22] (36%), m. p. 131—131·5°, sublimed at 130°/0·1 mm. (lit.,[22] m. p. 129°); nitro-[23] (20%), m. p. 158—159° (lit.,[23] m. p. 155°).

4-*Methoxytolan*.—Bromine (5·4 g.) in chloroform (50 c.c.) was added at 0° to 4-methoxystilbene (7·0 g.) in chloroform (100 c.c.). The precipitated 4-methylstilbene dibromide (10·2 g.) was collected and (1·5 g.) refluxed 2 hr. with 30% n-butanolic potassium hydroxide (15 c.c.). When cold, the whole was poured into ethanol–water (20 + 80 c.c.) and ether-extracted. Removal of solvents from the extracts then gave 4-*methoxytolan* (0·6 g., 56%), which crystallised from light petroleum (b. p. 60—80°) in plates, m. p. 58—60°, and sublimed at 60°/0·05 mm. (Found: C, 86·3; H, 6·1. $C_{15}H_{12}O$ requires C, 86·5; H, 5·8%).

Heating 4-methoxystilbene dibromide with aqueous potassium carbonate[3] gave, on cooling, a solid which was crystallised from ethanol and then sublimed in plates, m. p. 89—91° (reported[3] 89—90°) (Found: C, 79·4; H, 6·3. Calc. for $C_{15}H_{14}O_2$: C, 79·6; H, 6·2%). The *dinitrophenylhydrazone* of methoxydeoxybenzoin crystallised from benzene in red needles, m. p. 195° (Found: C, 62·7; H, 5·0; N, 13·6. $C_{21}H_{18}O_5N_4$ requires C, 62·1; H, 4·5; N, 13·8%).

4-*Methyltolan*.—Prepared by the recorded method,[21] this compound (40%) had m. p. 73—74° and sublimed at 75°/0·1 mm. (lit.,[21,24] m. p. 78—79°; 72·5—73·5°) (Found: C, 93·7; H, 6·2. Calc. for $C_{15}H_{12}$: C, 93·7; H, 6·3%).

4-*Chlorotolan*.—Prepared as for the methyl analogue,[19] the *tolan* (30%) separated from ethanol in plates, m. p. 83—84° (Found: C, 78·9; H, 4·7. $C_{14}H_9Cl$ requires C, 79·1; H, 4·3%).

4-*Nitrotolan*.—Bromine (3·7 g.) in chloroform (25 c.c.) was added at 65° to 4-nitrostilbene (4·6 g.) in chloroform (100 c.c.). On cooling, the crude 4-nitrostilbene dibromide [4·6 g., m. p. 203—205° (decomp.)] separated. The crude dibromide (2·75 g.) was added to potassium hydroxide (2 g.) in ethanol (100 c.c.), and the whole refluxed 30 min. On cooling, pouring into water, and ether extraction, there was obtained, from the extracts, a solid which was chromatographed on alumina. Elution with benzene gave initially 4-*nitrotolan* (0·134 g., 18%), which formed pale yellow plates (from ethanol), m. p. 120·5—121°, and sublimed at 120°/0·05 mm. (Found: C, 74·8; H, 4·1; N, 6·6. $C_{14}H_9O_2N$ requires C, 75·3; H, 4·1; N, 6·3%). Further elution with 1% ethyl acetate–benzene gave 4-nitrostilbene (0·094 g., 12%).

We thank Dr. N. Sheppard for reading the manuscript of this paper.

THE DYSON PERRINS LABORATORY, OXFORD.
THE UNIVERSITY CHEMICAL LABORATORY, CAMBRIDGE.
[*Received, June 16th*, 1959.]

---

[22] v. Walther and Raetze, *J. prakt. Chem.*, 1902, **65**, 283.
[23] Pfeiffer and Sergeiwskaya, *Ber.*, 1911, **44**, 1109.
[24] Scardiglia and Roberts, *Tetrahedron*, 1958, **3**, 197.