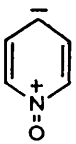
334. *The Electric Dipole Moments of a Series of 4-Substituted Pyridines and Pyridine 1-Oxides.*

By A. R. Katritzky, E. W. Randall, and L. E. Sutton.

The dipole moments of some compounds indicated in the title have been measured. Together with values for substituted alkanes and benzenes they afford evidence that the pyridine 1-oxide ring can create either a surfeit or deficit of electrons at the 4-position.

Linton [1] showed that the difference (2·02 D) between the dipole moments of pyridine 1-oxide (4·24 D) and pyridine (2·22 D) was much less than the difference (4·37 D) between the dipole moments of trimethylamine oxide (5·02 D) and trimethylamine (0·65 D), and pointed out that structures such as (I) must therefore be important contributors to the resonance hybrid of this molecule. Ochiai [2] and independently den Hertog and Overholt [3] demonstrated that this facilitated electrophilic substitution in the γ-position, and their observations have led to the opening of a new field of heterocyclic chemistry (for general review see ref. 4). Ochiai [2] later gave chemical evidence that structures such as (II) also contributed to the resonance hybrids of pyridine 1-oxides, but this has not yet been supported by dipole moment evidence. It was felt that comparison of the dipole moments of a series of substituted benzenes, pyridines, and pyridine 1-oxides might be illuminating.

(I)



(II)

Experimental

Preparation and Purification of Materials.—Benzene of analytical-grade was purified as described by Hill and Sutton.[5]

The preparation has already been described [6] of 4-chloro-, 4-acetyl-, and 4-ethoxycarbonyl-pyridine 1-oxide; the compounds were recrystallised two or three times more, immediately before measurement of their moments. The following preparation was more advantageous than that described [6] for 4-dimethylaminopyridine 1-oxide. 4-Chloropyridine 1-oxide (5 g.) and aqueous dimethylamine (30% w/v; 30 c.c.) were heated for 18 hr. (sealed tube). Potassium carbonate (5 g.) was added, the whole evaporated at 100°/14 mm., and the residue extracted with ethyl acetate. The extracts deposited 4-dimethylaminopyridine 1-oxide (93%), usually as a new *polymorph*, which after recrystallisation from ethanol–ethyl acetate

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[1] Linton, *J. Amer. Chem. Soc.*, 1940, **62**, 1945.

[2] Summarizing paper: Ochiai, *J. Org. Chem.*, 1953, **18**, 534.

[3] den Hertog and Overholt, *Rec. Trav. chim.*, 1950, **69**, 468.

[4] Katritzky, *Quart. Rev.*, 1956, **10**, 395.

[5] Hill and Sutton, *J.*, 1949, 746.

[6] Katritzky, *J.*, 1956, 2404.

TABLE 1.

4-Methoxypyridine 1-oxide

10^6w	ε	v	$10^5\Delta n_D$
547	2·2855	1·1444	6
1379	2·3033	1·1440	15
3246	2·3470	1·1432	36
6423	2·4184	1·1420	68
9494	2·4880	1·1407	101

$\varepsilon = 2\cdot2728 + 22\cdot68w$; $v = 1\cdot1446 - 0\cdot408w$; $\Delta n_D = 0\cdot00001 + 0\cdot106w$; ${}_EP = 34\cdot60$ c.c.; ${}_TP = 537\cdot45$ c.c.; $\mu = 5\cdot08 \pm 0\cdot01$ D.

4-Methylpyridine 1-oxide

10^6w	ε	v	$10^5\Delta n_D$
1358	2·3045	1·1442	14
3881	2·3609	1·1435	—
6115	2·4106	1·1427	60
7535	2·4443	1·1422	77

$\varepsilon = 2\cdot2731 + 22\cdot64w$; $v = 1\cdot1447 - 0\cdot321w$; $\Delta n_D = 0\cdot100w$; ${}_EP = 32\cdot61$ c.c.; ${}_TP = 492\cdot27$ c.c.; $\mu = 4\cdot74 \pm 0\cdot01$ D.

4-Dimethylaminopyridine 1-oxide *

10^6w	ε	v	$10^5\Delta n_D$
588	2·2939	1·1444	—
1147	2·3135	1·1442	—
1387	2·3236	1·1441	—

$\varepsilon = 2\cdot2726 + 36\cdot35w$; $v = 1\cdot1447 - 0\cdot421w$; ${}_EP = 43\cdot6$ c.c.; ${}_TP = 976\cdot0$ c.c.; $\mu = 6\cdot76 \pm 0\cdot04$ D.

4-Acetylpyridine 1-oxide

10^6w	ε	v	$10^5\Delta n_D$
2444	2·2934	1·1436	31
3896	2·3054	1·1432	48
6886	2·3317	1·1418	84
7933	2·3389	1·1416	99

$\varepsilon = 2\cdot2728 + 8\cdot413w$; $v = 1\cdot1446 - 0\cdot392w$; $\Delta n_D = 0\cdot00001 + 0\cdot122w$; ${}_EP = 39\cdot83$ c.c.; ${}_TP = 248\cdot89$ c.c.; $\mu = 3\cdot19 \pm 0\cdot02$ D.

4-Nitropyridine 1-oxide †

10^6w	ε	v	$10^5\Delta n_D$
635	2·2731	1·1443	9
667	2·2731	1·1442	—
992	2·2736	1·1441	13
1583	2·2737	1·1438	19
2004	2·2738	—	29
2050	2·2742	—	29
2077	2·2740	1·1436	—
2378	2·2743	—	30
5426	2·2768	1·1418	73
6238	2·2773	—	84
7837	2·2785	1·1406	103

$\varepsilon = 2\cdot2726 + 0\cdot751w$; $v = 1\cdot1446 - 0\cdot503w$; $\Delta n_D = 0\cdot00001 + 0\cdot130w$; ${}_EP = 36\cdot74$ c.c.; ${}_TP = 46\cdot59$ c.c.; $\mu = 0\cdot69 \pm 0\cdot02$ D.

4-Chloropyridine 1-oxide

10^6w	ε	v	$10^5\Delta n_D$
1725	2·2848	1·1439	14
3566	2·2979	1·1431	38
5782	2·3130	1·1421	57
7305	2·3235	1·1413	76

$\varepsilon = 2\cdot2729 + 6\cdot936w$; $v = 1\cdot1447 - 0\cdot462w$; $\Delta n_D = -0\cdot00003 + 0\cdot109w$; ${}_EP = 34\cdot01$ c.c.; ${}_TP = 196\cdot61$ c.c.; $\mu = 2\cdot82 \pm 0\cdot01$ D.

4-Ethoxycarbonylpyridine 1-oxide

10^6w	ε	v	$10^5\Delta n_D$
1255	2·2847	1·1442	11
3815	2·3093	1·1432	31
6020	2·3303	1·1426	48
8308	2·3523	1·1416	66

$\varepsilon = 2\cdot2727 + 9\cdot579w$; $v = 1\cdot1447 - 0\cdot363w$; $\Delta n_D = 0\cdot00001 + 0\cdot079w$; ${}_EP = 45\cdot83$ c.c.; ${}_TP = 341\cdot40$ c.c.; $\mu = 3\cdot80 \pm 0\cdot01$ D.

4-Dimethylaminopyridine

10^6w	ε	v	$10^5\Delta n_D$
1740	2·3012	1·1443	9
5339	2·3606	1·1436	38
6961	2·3874	1·1433	51
10,749	2·4530	1·1425	77

$\varepsilon = 2\cdot2721 + 16\cdot73w$; $v = 1\cdot1447 - 0\cdot209w$; $\Delta n_D = -0\cdot00003 + 0\cdot076w$; ${}_EP = 38\cdot82$ c.c.; ${}_TP = 419\cdot26$ c.c.; $\mu = 4\cdot31 \pm 0\cdot01$ D.

4-Acetylpyridine

10^6w	ε	v	$10^5\Delta n_D$
2110	2·2842	1·1442	6
8643	2·3188	1·1426	27
14,438	2·3496	1·1411	46
17,475	2·3657	1·1405	53

$\varepsilon = 2\cdot2728 + 5\cdot325w$; $v = 1\cdot1447 - 0\cdot242w$; $\Delta n_D = -0\cdot00001 + 0\cdot031w$; ${}_EP = 34\cdot22$ c.c.; ${}_TP = 154\cdot5$ c.c.; $\mu = 2\cdot41 \pm 0\cdot01$ D.

4-Nitropyridine

10^6w	ε	v	$10^5\Delta n_D$
2139	2·2778	1·1438	7
4100	2·2821	1·1420	12
7561	2·2900	1·1418	22
10,933	2·2975	1·1405	33

$\varepsilon = 2\cdot2728 + 2\cdot26w$; $v = 1\cdot1446 - 0\cdot381w$; $\Delta n_D = 0\cdot030w$; ${}_EP = 29\cdot92$ c.c.; ${}_TP = 82\cdot00$ c.c.; $\mu = 1\cdot58 \pm 0\cdot01$ D.

* Only three very dilute solutions of this compound could be obtained and so the error is larger than usual. The n_D values were not measured; ${}_EP$ was obtained as 44·42 c.c. from the measured mole refraction of 4-dimethylaminopyridine, 38·69 c.c., and the average increment for the N–O link, 5·74 c.c. This compares favourably with the 42·6 c.c. obtained from the values for dimethylaminobenzene, benzene, and pyridine 1-oxide, *viz.*, 40·8 c.c.,[a] 26·2 c.c.,[b] and 28 c.c. respectively.

† The error quoted is the precision error. The actual error is here liable to be much greater because of the effect of the neglect of ${}_AP$ upon a small moment. The ${}_AP$ term may be large since the molecule is comparable to *p*-dinitrobenzene and *p*-dicyanobenzene in having two large opposed group moments. *p*-Dinitrobenzene has an apparent moment of 0·63 D if the ${}_AP$ term of 8·2 c.c.[c] is taken as ${}_OP$. The figures for *p*-dicyanobenzene are 0·76 D and 11·9 c.c.,[c] respectively. The actual moment of 4-nitropyridine 1-oxide therefore appears to be indistinguishable from 0.

[a] Landolt and Börnstein, "Tabellen," Springer Verlag, Berlin, 1923, Vol. 1/2, p. 979. [b] *Op. cit.*, p. 977. [c] Coop and Sutton, *J.*, 1938, 1269.

had m. p. 223—225°. Sometimes partial melting occurred at 97°, with resolidification and then m. p. *ca.* 223° (Found : C, 60·6; H, 7·3. $C_7H_{10}ON_2$ requires C, 60·8; H, 7·1%).

The preparation of 4-acetylpyridine has also already been described;[7] refractionated, it had b. p. 91°/10 mm.

4-Methoxypyridine 1-oxide[2] was recrystallised four times from ethyl acetate and had m. p. 82—82·5° (lit.,[2] m. p. 81·5—82·5°).

4-Nitropyridine[2] was recrystallised three times from light petroleum (40—60°) and had m. p. 49·5—50·5° (lit.,[2] m. p. 50°).

4-Methylpyridine 1-oxide[8] was recrystallised three times from benzene and had m. p. 184—185° (lit.,[8, 9] m. p. 185—186° and 181°).

The following method was convenient for the preparation of 4-nitropyridine 1-oxide in large quantities : 30% aqueous hydrogen peroxide (100 c.c.) was added to pyridine (100 c.c.) in acetic acid (600 c.c.). The whole was heated for 24 hr. at 65—70°; more hydrogen peroxide (100 c.c.) was added, and the heating was repeated. The mixture was evaporated at 100°/14 mm. and the residue slowly added with cooling to a mixture of nitric acid (275 c.c.; *d* 1·5) and sulphuric acid (350 c.c.). The whole was heated for 12 hr. on the water-bath (nitrous fumes were evolved), cooled, and poured on ice (*ca.* 700 g.). Powdered anhydrous sodium carbonate (*ca.* 1200 g.) was added as rapidly as possible until effervescence ceased, and the whole was rapidly filtered. The solid was dried on the water-bath and extracted by refluxing chloroform (3 × 2 l.); evaporation of the extracts gave 4-nitropyridine 1-oxide (142—145 g., 82—85%), m. p. 153—158°. Two recrystallisations from acetone raised the m. p. to 159·5—160·5°, unchanged by further recrystallisation.

4-Dimethylaminopyridine was prepared by heating 4-dimethylaminopyridine 1-oxide (2·92 g.), acetic acid (8 c.c.), and iron filings (1·5 g.) on the water-bath for 1 hr. Excess of concentrated aqueous sodium hydroxide was added, the mixture filtered, and the filtrate extracted with chloroform. Removal of solvent gave the crude base (2·13 g., 83%) which after three crystallisations from ethyl acetate had m. p. 112—113° (Found : C, 68·6; H, 8·4. Calc. for $C_7H_{10}N_2$: C, 68·8; H, 8·2%) (lit.,[10] m. p. 114°).

Physical Measurements.—Electric dipole moments were determined by measuring the dielectric constants, specific volumes, and refractive indices for Na_D light of benzene solutions at 25°, using the methods described by Everard and Sutton[11] for their small-scale technique, with the heterodyne-beat capacitance meter described by Hill and Sutton.[12] The meter was calibrated by assuming the value 2·2727 for the dielectric constant of benzene at 25°.[13] The pyknometer was calibrated with air-free distilled water. The refractive-index difference, Δn_D, between the solution and benzene was measured with a Pulfrich refractometer.

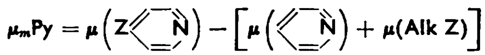
The computation of moments, and the notation used here, follow the pattern set by Everard, Hill, and Sutton,[14] so that no allowance has been made for atom polarisation, except where specifically stated, other than that implicit in using $[R]_D$ as the distortion polarisation. Other methods of calculating the slope, α, of the ε–w graphs, *e.g.*, that of Le Fèvre and Vine,[15] give moments which agree with those below to within the errors quoted. The results are given in Table 1.

DISCUSSION

Everard and Sutton[16] defined the mesomeric moment (μ_m) of an aromatic compound Ar–Z as the vector difference between its dipole moment and that of its aliphatic (preferably *tert.*-butyl) analogue Alk–Z. This quantity provides a measure of the interaction between the π-electron system of the aromatic ring and the group Z (with the limitations given by Everard and Sutton[17]).

[7] Katritzky, *J.*, 1955, 2587.
[8] Boeckelheide and Linn, *J. Amer. Chem. Soc.*, 1954, **76**, 1286.
[9] Ochiai, *J. Pharm. Soc. Japan*, 1944, **64**, 72.
[10] Koenigs, Friedrich, and Jurany, *Ber.*, 1925, **58**, 2571.
[11] Everard and Sutton, *J.*, 1951, 16.
[12] Hill and Sutton, *J.*, 1953, 1482.
[13] Hartshorn and Oliver, *Proc. Roy. Soc.*, 1929, *A*, **123**, 664.
[14] Everard, Hill, and Sutton, *Trans. Faraday Soc.*, 1950, **46**, 417.
[15] Le Fèvre and Vine, *J.*, 1937, 1805.
[16] Everard and Sutton, *J.*, 1951, 2818.
[17] *Idem*, *J.*, 1951, 2821.

Similarly the mesomeric moment of a substituted pyridine may be defined as :



The mesomeric moment (μ_mO) of a pyridine 1-oxide is defined analogously.

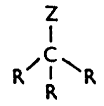
In pyridine the contribution of structure (III) to the resonance hybrid is far more important than that of structure (IV) (cf. the charge distribution [18]), hence it would be expected that the mesomeric moments (μ_mPy) of 4(γ)-derivatives of pyridine would be

(III)


(IV)

greater than those of the corresponding benzene derivatives when Z is an electron-donating group and less when Z is an electron-accepting group. If, however, in pyridine 1-oxide the contributions of both structures (I) and (II) are sufficiently great, then it might be predicted that the mesomeric moments of 4-substituted pyridine 1-oxides (μ_mO) are greater *in all cases* than those of the corresponding pyridines.

In order to calculate the mesomeric moments of a series of substituted benzenes, pyridines, and pyridine 1-oxides, the magnitudes and angles of the dipole moments of these compounds and of the corresponding substituted alkanes need to be known. Table 2 gives the magnitudes which have been measured or taken from the literature, and also the moment angles of the substituted alkanes and benzenes taken from the literature or



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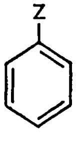

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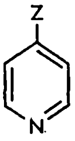

(VII)

(VIII)

A

calculated from published data. The convention here used to define moment angles is that in the compounds (V—VIII), if the moment points along the Z–C bond, Z being the positive end of the dipole, then it has angle 0° (*i.e.*, the angle is taken as in *A*).

The directions of the dipoles of the substituted pyridines and pyridine 1-oxides are not known, and in order to calculate the mesomeric moments, the reasonable assumption has been made that the mesomeric moments in benzene, pyridine, and pyridine 1-oxide have the same direction. This not only enables the mesomeric moments to be calculated, but also gives the directions of the dipole moments of the 4-substituted pyridines and pyridine 1-oxides. The results are recorded in Table 3.

The groups NMe_2, OMe, Cl, and Me all tend to donate electrons to the benzene ring in substituted benzenes (the angles of the mesomeric moments are all about 0°), and the tendency to donate is seen to decrease in the order given. In the pyridines, in each of these cases, the mesomeric moment is greater than in the corresponding benzene, as would be expected if canonical form (III) were important, and the mesomeric moments of the pyridine 1-oxides are greater still, demonstrating the importance of canonical forms such as (II).

The groups NO_2, COMe, and CO_2Et all attract electrons from the benzene nucleus (the angles of the mesomeric moments are all about 180°), and the attraction for electrons decreases in the order given. In the corresponding pyridines, the mesomeric moment is in each case less, as is expected because of the small importance of structures of type (IV) in pyridines. In the corresponding pyridine 1-oxides, however, the magnitude of the

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[18] Longuet-Higgins and Coulson, *Trans. Faraday Soc.*, 1947, **43**, 87.

TABLE 2.

Subst.	Moment magnitudes: 4-Substd. pyridine 1-oxide	4-Substd. pyridine	Substd. benzene	Substd. alkane	Moment angles: Substd. benzene	Subst. methane
H	4·24 ± 0·02 [b]	2·22 ± 0·02 [c]	0	0	—	—
Me	4·74 ± 0·01 [a]	2·61 ± 0·01 [c]	0·35 ± 0·05 [d]	0	0°	—
Cl	2·82 ± 0·01 [a]	0·78 ± 0·1 [c, k]	1·60 ± 0·01 [d]	2·01 ± 0·01 [d]	0	0°
OMe	5·08 ± 0·01 [a]	2·96 ± 0·01 [c]	1·28 ± 0·01 [21]	1·28 ± 0·01 [23]	80 [f]	124 [h]
NMe_2	6·76 ± 0·04 [a]	4·31 ± 0·01 [a]	1·61 ± 0·02 [d]	0·86 [d]	30 [d]	109 [j]
CO_2Et ...	3·80 ± 0·01 [a]	2·53 ± 0·04 [c]	1·85 [e]	1·8 [e]	110 [g]	89 [g]
COMe ...	3·19 ± 0·02 [a]	2·41 ± 0·01 [a]	2·96 ± 0·02 [d]	2·75 ± 0·05 [d]	131 [d]	120 [i]
NO_2	*ca.* 0	1·58 ± 0·01 [a]	4·01 ± 0·02 [d]	3·25 ± 0·05 [d]	180	180
CN	— [l]	1·65 ± 0·03 [c]	4·05 ± 0·01 [d]	3·60 ± 0·05 [d]	180	180

[a] Present investigation. [b] Linton's figures [1] recalculated. [c] Curran and Leis's figures [19] recalculated. [d] Taken from critical survey by Everard and Sutton.[20] [e] Selected as best available figures from data in Wesson's tables.[22] [f] With values of 2·08 (Leonard and Sutton's [24] value recalculated), 2·24 [25] and 2·23 D [26] for the dipole moments of *p*-fluoro-, *p*-chloro-, and *p*-bromo-anisole respectively, calculation by Hampson and Sutton's [27] method gave, respectively, values of 82°, 78·5°, and 78° for the moment angle in anisole.

[g] Difficulty was experienced in deducing these values. Use of Hampson and Sutton's [27] method gives discordant values: *e.g.*, Phalnikar, Bhide, and Nargund's values [28] for the moments of ethyl benzoate and its *p*-Cl, *p*-NO_2, and *p*-Br derivatives give values of 98°, 103°, and 102° respectively for the moment angle in ethyl benzoate, but Bergmann's value [29] for methyl *p*-bromobenzoate with the value for methyl benzoate [30] gives a value of 116° (no significant difference would be expected between the moment angles in ethyl and methyl benzoate). There appears to be no reliable way of deducing the direction of the moment in an aliphatic ester. In these circumstances the mesomeric moment of ethyl benzoate was assumed to be 0·50 D, at an angle of 180°, the justification being that the CO_2Et group is somewhat less electron-attracting than COMe [31] (with a μ_m in acetophenone of 0·56 D) and will have an angle near to 180°. By using these figures, it can be calculated that the moment angles in ethyl acetate and ethyl benzoate are respectively 89° and 105°. The former seems lower than would be expected, but the values are very susceptible to small differences in the assumptions made. Although the values of the mesomeric moments of 4-ethoxycarbonylpyridine and 4-ethoxycarbonylpyridine 1-oxide are also sensitive to the assumptions, it is at least clear that, provided μ_m for ethyl benzoate lies between 0·2 and 0·8 D, μ_mO in the *N*-oxide is appreciably larger than μ_mPy in the pyridine (thus if μ_m = 0·2 D, then μ_mPy = 0·03 D and μ_mO = 0·50 D, and if μ_m = 0·8 D, then μ_mPy = 0·69 D and μ_mO = 1·16 D).

[h] Calc. from $\angle$COC of 111° ± 3° in dimethyl ether.[32] [i] Calc. from $\angle$CCO of 120°.[33, 34] [j] Calc. from $\angle$CNC of 108° ± 4° in trimethylamine.[35] [k] An allowance of 4·9 c.c. has been made for ${}_AP$, since this is the sum of the ${}_AP$ terms for chlorobenzene (3·9 c.c.[36]) and pyridine (1·5 c.c.[37]) less the ${}_AP$ term for benzene (0·55 c.c.[37]). [l] Because of the very small solubility of this compound in benzene and the expectation of a small moment, the determination was not attempted.

moment (μ_mO) is again greater than that of the corresponding pyridine (μ_mPy), as one would expect if structures of type (I) were important (see Figure).

An alternative way of using the dipole moment data is to consider the vector difference μ_{NO} between the moment of a substituted pyridine 1-oxide and that of the corresponding pyridine. This will give the increase or decrease in the total moment due to the attachment of oxygen to nitrogen. By using the magnitudes and angles of the gross moments

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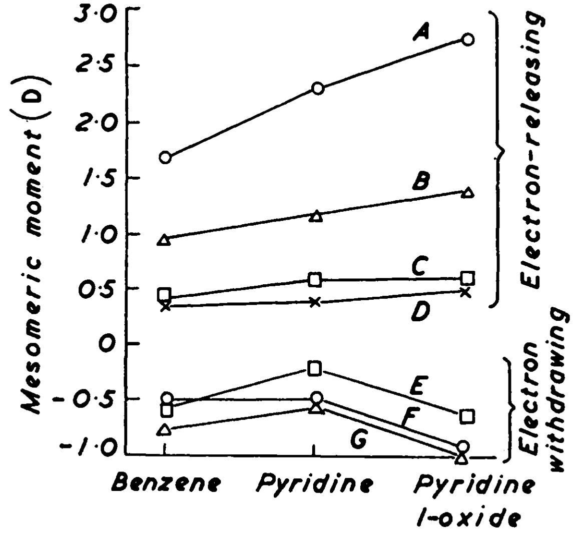
[19] Curran and Leis, *J. Amer. Chem. Soc.*, 1945, **67**, 79.
[20] Everard and Sutton, *J.*, 1951, 2807.
[21] *Idem, J.*, 1949, 2312.
[22] Wesson, "Tables of Electric Dipole Moments," The Technology Press, Massachusetts Institute of Technology, Cambridge, Mass., U.S.A., 1948.
[23] Groves and Sugden, *J.*, 1937, 1779.
[24] Leonard and Sutton, *J. Amer. Chem. Soc.*, 1948, **70**, 1564.
[25] Bergmann and Engel, *Z. phys. Chem.*, 1931, *B*, **15**, 85.
[26] Smyth and Walls, *J. Amer. Chem. Soc.*, 1932, **54**, 3230.
[27] Hampson and Sutton, *Proc. Roy. Soc.*, 1933, *A*, **140**, 561.
[28] Phalnikar, Bhide, and Nargund, *J. Univ. Bombay*, 1941, **10**, Pt. 3, 48.
[29] Bergmann, *J.*, 1936, 402.
[30] Phadke *et al.*, *J. Indian Chem. Soc.*, 1945, **22**, 235.
[31] Ingold, "Structure and Mechanism in Organic Chemistry," Bell, London, 1953, p. 77.
[32] Sutton and Brockway, *J. Amer. Chem. Soc.*, 1935, **57**, 473.
[33] Kimurn and Kurita, *J. Chem. Soc. Japan*, 1951, **72**, 3.
[34] Allen, Bowen, Sutton, and Bastiansen, *Trans. Faraday Soc.*, 1952, **48**, 991.
[35] Brockway and Jenkins, *J. Amer. Chem. Soc.*, 1936, **58**, 2036.
[36] Groves and Sugden, *J.*, 1934, 1094.
[37] Cartwright and Errera, *Proc. Roy. Soc.*, 1936, *A*, **154**, 138.

TABLE 3.

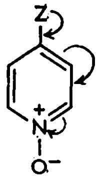
		Mesomeric moment magnitudes			Gross moment angles		
Subst.	Angle of mesomeric moment in substd. benzene	Substd. benzene	4-Substd. pyridine	4-Substd. pyridine 1-oxide	4-Substd. pyridine	4-Substd. pyridine 1-oxide	Vectorial diff. between pyridine 1-oxide and pyridine moments
NMe_2 ...	0°	1·66	2·27	2·74	11°	7°	2·51
OMe ...	12	0·96	1·16	1·39	27	16	2·25
Cl	0	0·41	0·57	0·59	0	0	2·06
Me	0	0·35	0·39	0·50	0	0	2·13
H	—	—	—	—	0	0	2·02
CO_2Et ...	180	0·50	0·47	0·93	45	28	1·55
COMe ...	166	0·56	0·21	0·62	75	45	1·63
NO_2	180	0·76	0·55	0·99	0	—	1·58
CN	180	0·45	0·27	—	0	—	—

of the pyridines and pyridine 1-oxides given in Tables 2 and 3, the values of μ_{NO} given in the last column of Table 3 have been found. These moments are all at an angle of 0° ± 1° (except for 3° in the case of the acetyl compounds) as would be expected. The magnitude

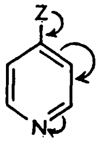


A, NMe_2; *B*, OMe; *C*, Cl; *D*, Me; *E*, COMe; *F*, CO_2Et; *G*, NO_2.

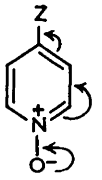
of 2·22 D for the difference between the moment of pyridine 1-oxide and pyridine is increased by electron-donating groups and decreased by electron-withdrawing groups. This shows that the electronic shifts indicated by the curved arrows are greater in structure (IX) than in (X) (Z being an electron-donating group) and greater in (XI) than in (XII) (Z being here an electron-accepting group).



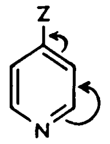
(IX)



(X)



(XI)



(XII)

Because electronic shifts of both type (IX—X) and type (XI—XII) are present simultaneously, and because it is impossible to calculate either separately, it should be considered whether the data might be explained by an alteration in either one or the other of these types of shift only. The two possibilities are: (i) A primary assumption that the difference in shifts (IX) and (X) is constant as Z changes. This would mean that when Z is an electron-attracting group, shift (XI) must be more sensitive to Z than shift (XII), which is reasonable. When, however, Z is an electron-donating group, the moment due to shift (XI) less shift (XII) would have to be smaller in the Z-substituted than in the unsubstituted compounds. This could arise only if the inductive effect of Z favoured (XII) over (XI); but in fact NMe_2, OMe, and Cl all would be expected to favour (XI) at least as much as (XII). (ii) The alternative primary assumption [that the importance of shifts (XI) and (XII) is constant] is very unlikely. Whereas (XII) is known to be small, because the mesomeric moments of the pyridines with electron-attracting substituents are smaller than those in the corresponding benzenes (Table 3), (XI) must be very large, as shown by Linton's work referred to in the first paragraph of this paper, and therefore more sensitive to Z. Therefore, neither single-shift explanation is satisfactory.

It is considered that the results just discussed show that the pyridine 1-oxide ring can create either a surfeit or a deficit of electrons in the 4-position; this is in accord with the chemical evidence which shows that under suitable conditions both electrophilic and nucleophilic reagents will attack the 4-position in pyridine 1-oxides.

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