891. *Electric Dipole Moments of Substituted Pyridines, Pyridine 1-Oxides, and Nitrobenzenes.*

By A. N. Sharpe and S. Walker.

Twenty-seven dipole moments have been measured of alkyl, phenyl, and halogenated derivatives of the nitrobenzene, pyridine, and pyridine 1-oxide systems in benzene solution at 25° ± 0·01°. The dipole moments of the pyridine 1-oxides are very dependent on atmospheric humidity; consistent results can only be obtained when moisture is rigorously excluded. The electron-accepting power of the ring is compared for the three ring systems and for benzene. Correlations have been made from certain physical data for these molecules with Hammett substituent constants and mesomeric moments. The importance of hyperconjugation in determining the dipole moment in such systems is considered.

Chemical and dipole-moment evidence [1-3] has shown that the N–O group in pyridine 1-oxide is considerably stabilised by resonance with the ring. *X*-Ray-diffraction work [4] has shown that the N–O bond in 4-nitropyridine 1-oxide has about 25% double-bond character, and the C–C bonds parallel to the longitudinal axis of the molecule about 90% double-bond character. In this particular molecule, therefore, the quinonoid structure is relatively important. Further, dipole-moment studies [3] showed that the mesomeric moment of pyridine 1-oxide is larger for both electron-withdrawing and electron-releasing substituents than in the pyridine or benzene series.

The possible modes of interaction of the polar group with the ring in nitrobenzene, pyridine, and pyridine 1-oxide present interesting comparisons, and it was felt that a study of ring-substituent interaction in these systems would be informative. In addition, a study of the dipole moments of homologous series of the alkyl derivatives of these systems and of benzene offered a means of investigating hyperconjugation in the different types of conjugated molecules.

Experimental

Apparatus and Techniques.—The heterodyne-beat apparatus and the method of measurement have been previously described.[5] Seven solutions were generally made up; the dielectric constant and specific volume of pure benzene were assumed to be 2·2725 and 1·14445 respectively. Deviations between these values and the extrapolated values from the graphs never exceeded ±0·0005 and ±0·00002, respectively. Calculation of dipole moments has also been described and the results are considered to be accurate to within ±0·01 D, unless otherwise stated.

Solutions of deliquescent pyridine 1-oxides were prepared in a glove box. Reproducible results were obtained only when a vigorous stream of dry nitrogen was passed for at least 0·5 hr. before exposure of the compound. Pure benzene was added from a separatory funnel which had a ground-glass joint fitting the bottle neck, a sintered-glass filter plug, and a soda-lime tube to admit air. Solutions were transferred to and from the dielectric constant cell under pressure of dry air, and the temperature of the bath was controlled within ±0·01°.

Preparation and Purification of Materials.—The purification of benzene has been described previously.[5]

The following compounds were prepared by known methods and purified by crystallisation or fractionation in a column of high efficiency and low hold-up. Values of m. p. or b. p. from the literature are given in parentheses: pyridine 1-oxide (from benzene or ether), m. p. 66—67°

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[1] Ochiai, summarizing paper, *J. Org. Chem.*, 1953, **18**, 534.
[2] Linton, *J. Amer. Chem. Soc.*, 1940, **62**, 1945.
[3] Katritzky, Randall, and Sutton, *J.*, 1957, 1769.
[4] Eichorn, *Acta Cryst.*, 1956, **9**, 787.
[5] Sharpe and Walker, *J.*, 1961, 2974.

(67° [6]); 4-methylpyridine 1-oxide (from benzene), m. p. 183° (185—186°,[7] 181° [8]), unchanged by further recrystallisation; 3-methylpyridine 1-oxide, m. p. 30°; 4-chloropyridine 1-oxide, (from acetone) m. p. 158° (decomp.), (from benzene), 149° (decomp.) (169·5°,[1] 152·5—153·5°,[9] 179·5—180° [10]); 4-bromopyridine 1-oxide (from acetone), m. p. 147° (decomp.), (from benzene), 142° (decomp.) [142—143°,[9] 163° (decomp.) [1]]; 3-chloropyridine 1-oxide b. p. 118—119°/1·05 mm., m. p. 54° (picrate, m. p. 141°); 3-bromopyridine 1-oxide, b. p. 124—126°/0·75 mm. (143—148°/4 mm.[11]), m. p. 43—44°; 3-iodopyridine 1-oxide (from benzene), m. p. 131° (picrate m. p. 145°); 4-bromopyridine,[12] distilled at −20° and evacuated at room temp.; 4-phenylpyridine 1-oxide [13] (from benzene), m. p. 151° (152—152·5° [13]); 3-chloropyridine, b. p.

TABLE 1.

Pyridine 1-*oxide* (*dry nitrogen*) *

10^6w_2	ε_{12}	v_{12}	n_{12}^2
1209	2·2964	1·14398	2·24385
2069	2·3139	1·14368	2·24415
3639	2·3452	1·14313	2·24464
3648	2·3467	1·14312	2·24468
6607	2·4058	1·14203	2·24553
7442	2·4235	1·14172	2·24577
9841	2·4716	1·14084	2·24661

$\varepsilon_{12} = 2{\cdot}2720 + 20{\cdot}232w_2$;
$v_{12} = 1{\cdot}14444 - 0{\cdot}3651w_2$;
$n_{12}^2 = 2{\cdot}24350 + 0{\cdot}3144w_2$; ${}_2P_\infty = 383{\cdot}95$ c.c.;
$R_D = 27{\cdot}36$ c.c.; $\mu = 4{\cdot}18$ D (ref. 2, 4·24).

* A second sample (see text) had the following values:
${}_2P_\infty = 387{\cdot}63$ c.c.; $R_D = 27{\cdot}81$ c.c.; $\mu = 4{\cdot}20$ D. The dipole moment was taken to be 4·19 D (4·24[2]).

4-*Propylpyridine* 1-*oxide* *

10^6w_2	ε_{12}	v_{12}	n_{12}^2
1053	2·2891	1·14422	2·24358
2513	2·3140	1·14388	2·24389
4338	2·3446	1·14346	2·24428
5201	2·3593	1·14323	2·24447
5230	2·3598	1·14324	2·24447
6275	2·3765	1·14298	2·24472
8305	2·4089	1·14252	2·24515

$\varepsilon_{12} = 2{\cdot}2721 + 16{\cdot}689w_2$;
$v_{12} = 1{\cdot}14446 - 0{\cdot}2336w_2$;
$n_{12}^2 = 2{\cdot}24335 + 0{\cdot}2170w_2$; ${}_2P_\infty = 467{\cdot}80$ c.c.;
$R_D = 42{\cdot}29$ c.c.; $\mu = 4{\cdot}56$ D.

* A sample of this compound made into solutions in partially dried air had $\mu = 4{\cdot}73$ D.

4-*t*-*Butylpyridine* 1-*oxide.*

10^6w_2	ε_{12}	v_{12}	n_{12}^2
555	2·2809	1·14434	2·24354
1274	2·2929	1·14419	2·24373
2656	2·3143	1·14389	2·24410
2747	2·3157	1·14388	2·24413
3682	2·3302	1·14368	2·24436
4262	2·3397	1·14355	2·24451
7187	2·3835	1·14293	2·24528

$\varepsilon_{12} = 2{\cdot}2725 + 15{\cdot}637w_2$:
$v_{12} = 1{\cdot}14446 - 0{\cdot}2145w_2$;
$n_{12}^2 = 2{\cdot}24340 + 0{\cdot}2622w_2$; ${}_2P_\infty = 486{\cdot}57$ c.c.;
$R_D = 48{\cdot}76$ c.c.; $\mu = 4{\cdot}63$ D.

4-*Ethylpyridine* 1-*oxide.*

10^6w_2	ε_{12}	v_{12}	n_{12}^2
816	2·2878	1·14420	2·24360
1351	2·2974	1·14406	2·24376
1841	2·3066	1·14392	2·24391
2819	2·3237	1·14367	2·24422
2874	2·3258	1·14363	2·24422
3525	2·3380	1·14345	2·24444
4737	2·3604	1·14308	2·24480

$\varepsilon_{12} = 2{\cdot}2725 + 18{\cdot}477w_2$;
$v_{12} = 1{\cdot}14444 - 0{\cdot}2817w_2$;
$n_{12}^2 = 2{\cdot}24334 + 0{\cdot}3086w_2$; ${}_2P_\infty = 459{\cdot}61$ c.c.;
$R_D = 38{\cdot}47$ c.c.; $\mu = 4{\cdot}54$ D.

4-*Isopropylpyridine* 1-*oxide* †

10^6w_2	ε_{12}	v_{12}	n_{12}^2
503	2·2815	1·14436	2·24341
1502	2·2985	1·14409	2·24365
3051	2·3241	1·14375	2·24400
3119	2·3259	1·14371	2·24403
3398	2·3308	1·14363	2·24409
4572	2·3492	1·14336	2·24436
8083	2·4088	1·14255	2·24520

$\varepsilon_{12} = 2{\cdot}2729 + 15{\cdot}931w_2$;
$v_{12} = 1{\cdot}14446 - 0{\cdot}2407w_2$;
$n_{12}^2 = 2{\cdot}24329 + 0{\cdot}2360w_2$; ${}_2P_\infty = 473{\cdot}75$ c.c.;
$R_D = 42{\cdot}49$ c.c.; $\mu = 4{\cdot}59$ D.

† A sample of this compound made into solutions in partially dried air had $\mu = 4{\cdot}74$ D.

3-*Methylpyridine* 1-*oxide* *

10^6w_2	ε_{12}	v_{12}	n_{12}^2
4110	2·3498	1·14323	2·24355
4863	2·3633	1·14304	2·24418
6716	2·4013	1·14244	2·24463
13,787	2·5346	1·14033	2·24533
21,071	2·6695	1·13822	2·24757
29,686	2·8363	1·13565	2·25024
50,824	3·2369	1·12945	2·25552

$\varepsilon_{12} = 2{\cdot}2725 + 18{\cdot}955w_2$;
$v_{12} = 1{\cdot}14444 - 0{\cdot}2954w_2$;
$n_{12}^2 = 2{\cdot}24235 + 0{\cdot}2638w_2$; ${}_2P_\infty = 416{\cdot}65$ c.c.;
$R_D = 32{\cdot}64$ c.c.; $\mu = 4{\cdot}33$ D.

* The weight fractions are unusually high for this investigation as a result of the deceptive appearance of the solid (additions to bottles in the glove-box cannot be weighed). The concentrations are within the limits used by many authors, and the linearity was excellent.

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[6] Rodd, " Chemistry of Carbon Compounds," Elsevier, Amsterdam, 1957, Vol. IVa.
[7] Boeckelheide and Linn, *J. Amer. Chem. Soc.*, 1954, **76**, 1286.
[8] Ochiai, *J. Pharm. Soc. Japan*, 1944, **64**, 72.
[9] den Hertog and Coombé, *Rec. Trav. chim.*, 1951, **70**, 581.
[10] Katritzky, *J.*, 1956, 2404.
[11] Murray and Hauser, *J. Org. Chem.*, 1954, **19**, 2008.
[12] Murray and Langham, *J. Amer. Chem. Soc.*, 1952, **74**, 6289.
[13] Katritzky and Hands, *J.*, 1958, 1754.

TABLE 1. (*Continued.*)

4-*Phenylpyridine* 1-*oxide*

10^6w_2	ε_{12}	v_{12}	n_{12}^2
888	2·2845	1·14414	2·24233
1690	2·2958	1·14385	2·24272
2501	2·3080	1·14352	2·24320
3552	2·3228	1·14312	2·24391
4443	2·3360	1·14279	2·24448
4646	2·3384	1·14269	2·24454
6943	2·3701	1·14187	2·24574

$\varepsilon_{12} = 2{\cdot}2723 + 14{\cdot}172w_2$;
$v_{12} = 1{\cdot}14447 - 0{\cdot}3775w_2$;
$n_{12}^2 = 2{\cdot}24178 + 0{\cdot}5863w_2$; ${}_2P_\infty = 492{\cdot}52$ c.c.;
$R_D = 57{\cdot}27$ c.c.; $\mu = 4{\cdot}61$ D.

4-*Chloropyridine* 1-*oxide*

10^6w_2	ε_{12}	v_{12}	n_{12}^2
1680	2·2844	1·14373	2·24290
2107	2·2875	1·14348	2·24314
3580	2·2975	1·14289	2·24352
3945	2·3003	1·14273	2·24382
5589	2·3116	1·14195	2·24415
5977	2·3149	1·14180	2·24433
6471	2·3178	1·14159	2·24463

$\varepsilon_{12} = 2{\cdot}2725 + 7{\cdot}034w_2$;
$v_{12} = 1{\cdot}14445 - 0{\cdot}4442w_2$;
$n_{12}^2 = 2{\cdot}24239 + 0{\cdot}3279w_2$; ${}_2P_\infty = 198{\cdot}42$ c.c.;
$R_D = 34{\cdot}68$ c.c.; $\mu = 2{\cdot}83$ D (ref. 3, 2·82).

3-*Chloropyridine* 1-*oxide*

10^6w_2	ε_{12}	v_{12}	n_{12}^2
2141	2·2976	1·14350	2·24397
2932	2·3073	1·14311	2·24424
4853	2·3295	1·14228	2·24502
4938	2·3309	1·14221	2·24505
7003	2·3545	1·14131	2·24577
8262	2·3688	1·14073	2·24619
10,575	2·3957	1·13971	2·24691

$\varepsilon_{12} = 2{\cdot}2726 + 11{\cdot}697w_2$;
$v_{12} = 1{\cdot}14445 - 0{\cdot}4496w_2$;
$n_{12}^2 = 2{\cdot}24325 + 0{\cdot}3538w_2$; ${}_2P_\infty = 311{\cdot}81$ c.c.;
$R_D = 35{\cdot}12$ c.c.; $\mu = 3{\cdot}68$ D.

3-*Iodopyridine* 1-*oxide*

10^6w_2	ε_{12}	v_{12}	n_{12}^2
1725	2·2854	1·14321	2·24337
1938	2·2868	1·14310	2·24334
2039	2·2872	1·14307	2·24334
5789	2·3159	1·14034	2·24460
7373	2·3267	1·13930	2·24475
8859	2·3373	1·13829	2·24523
15,259	2·3856	1·13376	2·24718

$\varepsilon_{12} = 2{\cdot}2725 + 7{\cdot}385w_2$;
$v_{12} = 1{\cdot}14445 - 0{\cdot}6998w_2$;
$n_{12}^2 = 2{\cdot}24276 + 0{\cdot}2906w_2$; ${}_2P_\infty = 336{\cdot}21$ c.c.;
$R_D = 41{\cdot}04$ c.c.; $\mu = 3{\cdot}79$ D.

3-*Ethylpyridine*

10^6w_2	ε_{12}	v_{12}	n_{12}^2
1695	2·2831	1·14431	2·24260
4192	2·2976	1·14413	2·24254
5523	2·3052	1·14403	2·24257
8399	2·3218	1·14381	2·24257
9075	2·3259	1·14377	2·24260
12,686	2·3468	1·14349	2·24257
14,234	2·3565	1·14337	2·24251

$\varepsilon_{12} = 2{\cdot}2730 + 5{\cdot}840w_2$;
$v_{12} = 1{\cdot}14444 - 0{\cdot}0747w_2$;
$n_{12}^2 = 2{\cdot}24258 - 0{\cdot}002w_2$; ${}_2P_\infty = 151{\cdot}81$ c.c.;
$R_D = 33{\cdot}54$ c.c.; $\mu = 2{\cdot}41$ D.

4-*Methylpyridine* 1-*oxide*

10^6w_2	ε_{12}	v_{12}	n_{12}^2
785	2·2882	1·14417	2·24421
1479	2·3033	1·14394	2·24445
1823	2·3101	1·14381	2·24451
2727	2·3292	1·14357	2·24495
2875	2·3317	1·14352	2·24505
3242	2·3388	1·14340	2·24517
4491	2·3644	1·14303	2·24565

$\varepsilon_{12} = 2{\cdot}2725 + 20{\cdot}560w_2$;
$v_{12} = 1{\cdot}14442 - 0{\cdot}3163w_2$;
$n_{12}^2 = 2{\cdot}24384 + 0{\cdot}4052w_2$; ${}_2P_\infty = 448{\cdot}90$ c.c.;
$R_D = 34{\cdot}92$ c.c.; $\mu = 4{\cdot}50$ D (ref. 3, 4·74).

4-*Bromopyridine* 1-*oxide*

10^6w_2	ε_{12}	v_{12}	n_{12}^2
1078	2·2786	1·14377	2·24270
1644	2·2815	1·14344	2·24290
2709	2·2878	1·14281	2·24313
3158	2·2897	1·14255	2·24327
3567	2·2919	1·14224	2·24335
6006	2·3053	1·14080	2·24403
6455	2·3086	1·14045	2·24412

$\varepsilon_{12} = 2{\cdot}2726 + 5{\cdot}492w_2$;
$v_{12} = 1{\cdot}14445 - 0{\cdot}6130w_2$;
$n_{12}^2 = 2{\cdot}24243 + 0{\cdot}2640w_2$; ${}_2P_\infty = 207{\cdot}29$ c.c.;
$R_D = 35{\cdot}85$ c.c.; $\mu = 2{\cdot}90$ D.

3-*Bromopyridine* 1-*oxide*

10^6w_2	ε_{12}	v_{12}	n_{12}^2
1540	2·2854	1·14352	2·24370
2143	2·2917	1·14317	2·24373
3029	2·2990	1·14263	2·24412
3959	2·3066	1·14205	2·24430
5976	2·3251	1·14086	2·24493
7535	2·3379	1·13986	2·24532
9197	2·3537	1·13881	2·24574

$\varepsilon_{12} = 2{\cdot}2724 + 8{\cdot}776w_2$;
$v_{12} = 1{\cdot}14446 - 0{\cdot}6088w_2$;
$n_{12}^2 = 2{\cdot}24323 + 0{\cdot}2765w_2$; ${}_2P_\infty = 314{\cdot}65$ c.c.;
$R_D = 36{\cdot}49$ c.c.; $\mu = 3{\cdot}69$ D.

3-*Methylpyridine*

10^6w_2	ε_{12}	v_{12}	n_{12}^2
2181	2·2872	1·14426	2·24276
3424	2·2956	1·14413	2·24274
5835	2·3116	1·14387	2·24274
6438	2·3163	1·14385	2·24280
7108	2·3208	1·14377	2·24276
11,181	2·3483	1·14335	2·24281
12,455	2·3571	1·14320	2·24284

$\varepsilon_{12} = 2{\cdot}2725 + 6{\cdot}775w_2$;
$v_{12} = 1{\cdot}14447 - 0{\cdot}1000w_2$;
$n_{12}^2 = 2{\cdot}24271 + 0{\cdot}008w_2$; ${}_2P_\infty = 147{\cdot}63$ c.c.;
$R_D = 28{\cdot}50$ c.c.; $\mu = 2{\cdot}41$ D.*

* Lit., (*a*) 2·40, (*b*) 2·30 D. (For refs. see p. 4526.)

3-*Isopropylpyridine*

10^6w_2	ε_{12}	v_{12}	n_{12}^2
1429	2·2796	1·14437	2·24247
2963	2·2880	1·14428	2·24242
4509	2·2957	1·14417	2·24233
6002	2·3034	1·14408	2·24230
7218	2·3101	1·14399	2·24224
8723	2·3183	1·14390	2·24221
12,408	2·3372	1·14366	2·24207

$\varepsilon_{12} = 2{\cdot}2723 + 5{\cdot}230w_2$;
$v_{12} = 1{\cdot}14446 - 0{\cdot}0638w_2$;
$n_{12}^2 = 2{\cdot}24253 - 0{\cdot}039w_2$; ${}_2P_\infty = 158{\cdot}20$ c.c.;
$R_D = 37{\cdot}45$ c.c.; $\mu = 2{\cdot}43$ D.

TABLE 1. (*Continued*).

4-*Phenylpyridine*

10^6w_2	ε_{12}	v_{12}	n_{12}^2
1008	2·2772	1·14427	2·24227
1617	2·2806	1·14412	2·24240
3216	2·2881	1·14369	2·24278
4682	2·2948	1·14339	2·24326
5353	2·2984	1·14317	2·24349
7781	2·3097	1·14260	2·24427
8688	2·3147	1·14238	2·24433

$\varepsilon_{12} = 2{\cdot}2725 + 4{\cdot}823w_2;$
$v_{12} = 1{\cdot}14446 - 0{\cdot}2350w_2;$
$n_{12}^2 = 2{\cdot}24192 + 0{\cdot}2745w_2;\ {}_2P_\infty = 182{\cdot}81$ c.c.;
$R_\text{D} = 50{\cdot}16$ c.c.; $\mu = 2{\cdot}55$ D.

3-*Chloropyridine*

10^6w_2	ε_{12}	v_{12}	n_{12}^2
1824	2·2800	1·14387	2·24340
3626	2·2871	1·14331	2·24344
4785	2·2919	1·14296	2·24346
7411	2·3022	1·14213	2·24372
8377	2·3059	1·14183	2·24378
9516	2·3015	1·14145	2·24388
14,660	2·3308	1·13984	2·24416

$\varepsilon_{12} = 2{\cdot}2726 + 3{\cdot}988w_2;$
$v_{12} = 1{\cdot}14445 - 0{\cdot}3139w_2;$
$n_{12}^2 = 2{\cdot}24320 + 0{\cdot}0685w_2;\ {}_2P_\infty = 113{\cdot}26$ c.c.;
$R_\text{D} = 29{\cdot}12$ c.c.; $\mu = 2{\cdot}02$ D.*

* Lit,[d] 2·02 D (for ref. see p. 4526).

3-*Iodopyridine*

10^6w_2	ε_{12}	v_{12}	n_{12}^2
719	2·2740	1·14397	2·24188
2332	2·2773	1·14299	2·24221
2535	2·2779	1·14284	2·24224
3802	2·2805	1·14199	2·24245
4046	2·2812	1·14192	2·24245
4556	2·2824	1·14158	2·24257
7633	2·2888	1·13964	2·24316

$\varepsilon_{12} = 2{\cdot}2724 + 2{\cdot}154w_2;$
$v_{12} = 1{\cdot}14442 - 0{\cdot}6249w_2;$
$n_{12}^2 = 2{\cdot}24174 + 0{\cdot}187w_2;\ {}_2P_\infty = 114{\cdot}79$ c.c.;
$R_\text{D} = 38{\cdot}50$ c.c.; $\mu = 1{\cdot}93$ D.

m-*Chloronitrobenzene*

10^6w_2	ε_{12}	v_{12}	n_{12}^2
1034	2·2811	1·14405	2·24356
1894	2·2885	1·14368	2·24380
3514	2·3009	1·14299	2·24397
4621	2·3106	1·14251	2·24406
5961	2·3220	1·14197	2·24436
7490	2·3342	1·14132	2·24454
7839	2·3376	1·14118	2·24463

$\varepsilon_{12} = 2{\cdot}2725 + 8{\cdot}265w_2;$
$v_{12} = 1{\cdot}14447 - 0{\cdot}4201w_2;$
$n_{12}^2 = 2{\cdot}24347 + 0{\cdot}143w_2;\ {}_2P_\infty = 278{\cdot}93$ c.c.;
$R_\text{D} = 37{\cdot}74$ c.c.; $\mu = 3{\cdot}44$ D.*

* Lit.,[b] 3·38, 3·18, 3·12, 3·40 D.

4-*Bromopyridine* *

10^6w_2	ε_{12}	v_{12}	n_{12}^2
1427	2·2734	1·14371	2·24308
3196	2·2747	1·14272	2·24343
3465	2·2750	1·14250	2·24349
4361	2·2755	1·14213	2·24358
7500	2·2773	1·14040	2·24400
11,220	2·2801	1·13850	2·24454
19,088	2·2849	1·13436	2·24565

$\varepsilon_{12} = 2{\cdot}2726 + 0{\cdot}6507w_2;$
$v_{12} = 1{\cdot}14444 - 0{\cdot}5325w_2;$
$n_{12}^2 = 2{\cdot}24295 + 0{\cdot}1414w_2;\ {}_2P_\infty = 48{\cdot}14$ c.c.;
$R_\text{D} = 32{\cdot}59$ c.c.; $\mu = 0{\cdot}77 \pm 0{\cdot}02$ D (0·79).†

* An allowance of 4·9 c.c. was made by Katritzky, Randall, and Sutton[3] for the P_A of 4-chloropyridine, being the sum of the P_A terms for chlorobenzene (3·9 c.c.) and pyridine (1·5 c.c.) less the P_A term for benzene (0·55 c.c.). A similar allowance of 3·5 c.c. was made for the P_A of 4-bromopyridine, from the P_A of bromobenzene (2·5 c.c.) (ref. *c*, p. 4526).

† Cumper and Vogel's figure[d] recalculated by taking $P_\text{A} = 3{\cdot}5$ c.c.

3-*Bromopyridine*

10^6w_2	ε_{12}	v_{12}	n_{12}^2
945	2·2751	1·14396	2·24287
1880	2·2775	1·14343	2·24302
3901	2·2833	1·14240	2·24311
5571	2·2881	1·14150	2·24337
6446	2·2907	1·14104	2·24358
8492	2·2964	1·13996	2·24364
11,243	2·3044	1·13848	2·24400

$\varepsilon_{12} = 2{\cdot}2722 + 2{\cdot}861w_2;$
$v_{12} = 1{\cdot}14445 - 0{\cdot}5997w_2;$
$n_{12}^2 = 2{\cdot}24275 + 0{\cdot}113w_2;\ {}_2P_\infty = 113{\cdot}97$ c.c.;
$R_\text{D} = 31{\cdot}86$ c.c.; $\mu = 2{\cdot}00$ D.*

* Lit., (*d*) 2·02, (*e*) 1·93 D (for refs. see p. 4526).

p-*Chloronitrobenzene*

10^6w_2	ε_{12}	v_{12}	n_{12}^2
732	2·2759	1·14415	2·24304
2095	2·2822	1·14360	2·24319
3683	2·2908	1·14288	2·24334
4509	2·2937	1·14255	2·24349
5886	2·3009	1·14198	2·24367
5897	2·3011	1·14197	2·24367
10,459	2·3227	1·14007	2·24418

$\varepsilon_{12} = 2{\cdot}2724 + 4{\cdot}825w_2;$
$v_{12} = 1{\cdot}14445 - 0{\cdot}4194w_2;$
$n_{12}^2 = 2{\cdot}24293 + 0{\cdot}122w_2;\ {}_2P_\infty = 177{\cdot}02$ c.c.;
$R_\text{D} = 37{\cdot}15$ c.c.; $\mu = 2{\cdot}62$.*

* Lit.,[b] 2·52, 2·55, 2·36, 2·34, 2·57, 3·12 D (for ref. see p. 4526).

p-*Bromonitrobenzene*

10^6w_2	ε_{12}	v_{12}	n_{12}^2
903	2·2760	1·14395	2·24328
2332	2·2816	1·14312	2·24354
3033	2·2846	1·14266	2·24370
3776	2·2875	1·14222	2·24382
4997	2·2921	1·14157	2·24421
7166	2·3010	1·14035	2·24466
7923	2·3039	1·13985	2·24478

$\varepsilon_{12} = 2{\cdot}2722 + 4{\cdot}026w_2;$
$v_{12} = 1{\cdot}14445 - 0{\cdot}5785w_2;$
$n_{12}^2 = 2{\cdot}24306 + 0{\cdot}218w_2;\ {}_2P_\infty = 187{\cdot}02$ c.c.;
$R_\text{D} = 41{\cdot}90$ c.c.; $\mu = 2{\cdot}66$ D.*

* Lit.,[b] 2·69, 2·53, 2·45, 2·65 D (for ref. see p. 4526).

TABLE 1. (*Continued.*)

m-*Bromonitrobenzene*

10^6w_2	ε_{12}	v_{12}	n_{12}^2
2048	2·2855	1·14332	2·24305
3104	2·2924	1·14270	2·24326
4345	2·3005	1·14200	2·24348
5861	2·3108	1·14112	2·24364
7445	2·3207	1·14026	2·24393
7552	2·3216	1·14009	2·24393
9422	2·3332	1·13906	2·24421

$\varepsilon_{12} = 2{\cdot}2722 + 6{\cdot}519w_2$;
$v_{12} = 1{\cdot}14448 - 0{\cdot}5735w_2$;
$n_{12}^2 = 2{\cdot}24271 + 0{\cdot}164w_2$; ${}_2P_\infty = 282{\cdot}05$ c.c.;
$R_D = 40{\cdot}12$ c.c.; $\mu = 3{\cdot}44$ D.*

† Lit.,^{b} 3·17, 3·41 (for ref. see p. below).

m-*Iodonitrobenzene*

10^6w_2	ε_{12}	v_{12}	n_{12}^2
650	2·2759	1·14401	2·24337
2202	2·2846	1·14301	2·24364
3199	2·2900	1·14235	2·24385
3963	2·2945	1·14185	2·24400
9462	2·3254	1·13824	2·24493
10,635	2·3320	1·13743	2·24511
11,314	2·3358	1·13706	2·24524

$\varepsilon_{12} = 2{\cdot}2722 + 5{\cdot}619w_2$;
$v_{12} = 1{\cdot}14445 - 0{\cdot}6579w_2$;
$n_{12}^2 = 2{\cdot}24328 + 0{\cdot}173w_2$; ${}_2P_\infty = 299{\cdot}27$ c.c.;
$R_D = 43{\cdot}73$ c.c.; $\mu = 3{\cdot}54$ D.*

* Lit.,^{b} 3·22, 3·62 D (for ref. see below).

p-*Iodonitrobenzene*

10^6w_2	ε_{12}	v_{12}	n_{12}^2
1687	2·2793	1·14340	2·24225
2332	2·2815	1·14292	2·24253
3761	2·2872	1·14202	2·24281
5219	2·2929	1·14106	2·24323
6286	2·2968	1·14036	2·24343
7705	2·3025	1·13935	2·24373
8470	2·3055	1·13890	2·24397

$\varepsilon_{12} = 2{\cdot}2725 + 3{\cdot}897w_2$;
$v_{12} = 1{\cdot}14446 - 0{\cdot}6546w_2$;
$n_{12}^2 = 2{\cdot}24190 + 0{\cdot}244w_2$; ${}_2P_\infty = 218{\cdot}87$ c.c.;
$R_D = 47{\cdot}33$ c.c.; $\mu = 2{\cdot}90$ D.*

† Lit.,^{b} 3·04, 2·63 D (for ref. see below).

Refs.: (*a*) Cumper, Vogel, and Walker, *J.*, 1956, 3621. (*b*) Wesson, " Tables of Electric Dipole Moments," Technology Press, Cambridge, Mass. (*c*) Huang and Sullivan, *Nature*, 1960, **188**, 1104. (*d*) Cumper and Vogel, *J.*, 1960, 4723. (*e*) Goethals, *Rec. Trav. chim.*, 1935, **54**, 299.

147·5°/754 mm. (148°/744 mm.[14]); 3-bromopyridine,[15] b. p. 171°/751 mm. (169—170° [14], 173° [14], 173·7—174°/762 mm.[15]); 3-iodopyridine,[16] m. p. 53—54° (52° [16], 53·5° [14]); 3-isopropylpyridine,[17] b. p. 179°/750 mm. (179·3° [17]) [picrate, m. p. 138·5° (138·1—138·6° [17])].

The halogenonitrobenzenes were commercial samples or prepared by diazotisation. All were steam-distilled and fractionally crystallised from light petroleum: *m*-chloro-, m. p. 45·5° (46° [14]), *m*-bromo-, m. p. 56·5° (56° [14]), *m*-iodo-, m. p. 38° (38·5° [14]), *p*-chloro-, m. p. 83° (83° [14]), *p*-bromo-, m. p. 127° (127° [14]), and *p*-iodo-nitrobenzene, m. p. 174·5° (174° [14]).

Solid samples were stored under a high vacuum in the presence of phosphoric oxide and wax shavings in the dark for at least 2 days before use. For deliquescent compounds the desiccator was refilled with dry nitrogen. Liquids were used immediately after distillation, or, where this was impossible, were stored in the dark in small Quickfit stoppered flasks with a minimum of air space.

DISCUSSION

The two results for pyridine 1-oxide, which are for different samples, one crystallised from benzene and weighed out in an atmosphere of nitrogen, and the other crystallised from ether and weighed out in an atmosphere of carefully dried air, are identical within the limits of experimental error, but differ significantly from the value obtained by Linton,[2] who stated that drying trains were used but did not stress the importance of exclusion of moisture. The difference (0·23 D) between the value for 4-methylpyridine 1-oxide and that obtained by Katritzky, Randall, and Sutton [3] is probably due to the effect of water; no mention of special precautions was made in their paper; the value obtained for 4-chloropyridine 1-oxide, which is not particularly hygroscopic, is identical within the limits of

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[14] Heilbron, " Dictionary of Organic Compounds," Eyre and Spottiswoode, London, 1936.
[15] den Hertog and Wibaut, *Rec. Trav. chim.*, 1932, **51**, 949.
[16] Gergely and Iredale, *J.*, 1953, 3232.
[17] Brown and Murphey, *J. Amer. Chem. Soc.*, 1951, **73**, 3308.

experimental error with the value obtained by these workers. The water probably exerts its effect by forming a highly polar hydroxide. No changes were observed under differing conditions with the substituted pyridines and nitrobenzenes.

TABLE 2.

Comparison of moments calculated with and without inclusion of the inductive effect.

Subst.	$\mu_{\text{obs.}}$	$\mu_{\text{calc.}}$*	$\mu_{\text{corr.}}$†	Subst.	$\mu_{\text{obs.}}$	$\mu_{\text{calc.}}$*	$\mu_{\text{corr.}}$†
			Nitrobenzene				
3-Me	4·14	4·21	4·28	4-Me	4·42	4·38	4·44
3-Cl	3·44	3·50	3·50	4-Bu^t	4·61	4·46	4·58
3-Br	3·44	3·50	3·51	4-Cl	2·62	2·43	2·46
3-I	3·54	3·52	3·57	4-Br	2·66	2·45	2·51
				4-Ph	4·36	4·01	4·18
			Pyridine				
3-Me	2·41	2·42	2·46	4-Me	2·60	2·59	2·63
3-Cl	2·02	1·98	1·96	4-Bu^t	2·73	2·66	2·75
3-Br	2·00	1·98	1·96	4-Cl	0·78	0·64	0·67
3-I	1·93	1·94	1·92	4-Br	0·77	0·66	0·70
				4-Ph	2·55	2·21	2·32
			Pyridine 1-oxide				
3-Me	4·33	4·37	4·45	4-Me	4·50	4·55	4·63
3-Cl	3·69	3·66	3·66	4-Bu^t	4·63	4·64	4·80
3-Br	3·69	3·65	3·67	4-Cl	2·83	2·60	2·65
3-I	3·79	3·68	3·71	4-Br	2·90	2·62	2·69
				4-Ph	4·62	4·19	4·38

* Calc. without inclusion of the inductive effect.
† Calc. with inclusion of the inductive effect.

The bond lengths and angles in pyridine (and presumably pyridine 1-oxide) differ from those in benzene.[18] This difference is certain to mean differing electronegativities of the ring-carbon atoms in the two systems, and this in turn will affect both the C–X moment and the unsubstituted C–H moments. It would, thus, be unwise to expect the calculated moment, even for a substituent with a low mesomeric and induced moment, to be identical with the observed moment.

In Table 2 values obtained by summation of the moments of the parent compounds and the corresponding substituted benzenes ($\mu_{\text{calc.}}$) are compared with values obtained by allowing for the classical inductive effect ($\mu_{\text{corr.}}$) in a way similar to that used by Smith and Littlejohn for monosubstituted biphenyls.[19]

The dipole moment induced in a substituent by a dipole μ may be estimated from the equations: [20]

$$\mu_x = \frac{\mu\gamma(\varepsilon_b + 2)}{3\varepsilon_a r^3}\,(3\cos^2\theta - 1)$$

$$\mu_y = \frac{\mu\gamma(\varepsilon_b + 2)}{\varepsilon_a r^3}\cdot\sin\theta\cos\theta$$

where μ_x and μ_y are the moments induced along the x and the y axis, respectively, in the plane containing the polarisable centre and the polarising dipole, the line from the polarisable centre to the dipole being inclined at an angle θ to the axis of the dipole: ε_a is the dielectric constant of the material between the dipole and the polarisable centre, and ε_b the dielectric constant of the polarisable material. Both ε_a and ε_b were taken as 2·3, the dielectric constant of benzene, and the polarisabilities γ were calculated from the appropriate bond refractions.[21] In the case of pyridine, the polarising dipole was

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[18] Bak, Hansen, and Rastrup-Anderson, *J. Chem. Phys.*, 1954, **22**, 2013.

[19] Smith and Littlejohn, *J.*, 1953, 2456; 1954, 2552.

[20] Smith, " Electric Dipole Moments," Butterworths, London, 1955.

[21] Smallwood and Herzfeld, *J. Amer. Chem. Soc.*, 1930, **52**, 1919.

assumed to be situated in the region of the nitrogen atom and to be about 1·8 D.[22] Three sets of values, corresponding to a polarising dipole located up to 0·2 Å from the nitrogen atom did not differ by more than 0·01 D.

Except for alkyl compounds, the moments calculated with inclusion of the inductive effect are generally closer to the observed values than those without, although the agreement is still not good. The calculated moments of the alkyl compounds are, in general, larger than the observed moments, the remainder generally smaller.

Chemical and previous dipole-moment evidence indicates that the mesomeric effect of substituents attached to the pyridine ring is higher for electron-releasing and lower for electron-withdrawing substituents than in the benzene series, and that it is greater for both types of substituent in the 4-position of pyridine 1-oxide than in the pyridine or benzene series. This conclusion is supported by infrared work.[23] The results in the present work, which are only for electron-releasing substituents, or substituents whose mesomeric moment is directed towards the ring, agree with such conclusions. In addition, the interaction moments in Table 3, which reflect changes in induced and mesomeric moments relative to the corresponding groups in benzene, indicate that the electron-accepting power of the nitrobenzene ring lies between those of pyridine and pyridine 1-oxide.

Estimates have been made of the C–H bond moment in pyridine and benzene [24] but cannot yet be made for pyridine 1-oxide, and the $\mu_{\text{int.}}$ values are dependent on the C–H bond moment differences in these systems. This is borne out by the relative order of the interaction moments for the alkyl substituents, which for these dipoles of small magnitude suggests that the values are governed by C–H bond-moment variations. The values of $\mu_{\text{CX}} - \mu_{\text{CH}}$ (see Table 4) indicate a similar order of electron-accepting power. When the calculated induced moments are allowed for, the order is unchanged.

TABLE 3.

Interaction moments [a] (D) ($\mu_{\text{int.}} = \mu_{\text{obs.}} - \mu_{\text{calc.}}$).

4-Subst.	Benzene	Pyridine	Nitrobenzene	Pyridine 1-oxide
NO_2	0	+0·22 [b]	—	+0·51 [b, e]
CN	0	+0·17 [b]	—	—
Cl	0	+0·15 [b]	+0·19 [c]	+0·22 [c]
Br	0	+0·12 [c]	+0·21 [c]	+0·27 [c]
Me	0	+0·02 [d]	+0·04 [a]	−0·06 [c]
Bu^t	0	+0·07 [d]	+0·15 [f]	+0·01 [c]
Ph	0	+0·34 [a]	+0·35 [a]	+0·42 [c]
MeO	0	+0·14 [b]	+0·32 [a]	+0·40 [b]
NMe_2	0	+0·95 [b]	+1·48 [a]	+1·52 [b]

[a] Bond angles and moments used in obtaining $\mu_{\text{int.}}$ were taken from Smith (ref. 20, p. 209). [b, d, f] Observed values from refs. 3, 24, and 23, respectively. [c] This investigation. [e] $\mu_{\text{obs.}}$ taken as 0·69 D; [3] this is probably too high through neglect of P_A, and the workers suggest that the actual moment is indistinguishable from zero.

Since Hammett substituent constants are a measure of the interaction between a substituent and the ring, linear relations are frequently found between the σ values and sets of physical data.[25,26] A linear relation between dipole moments and σ value for *para*- and apparently also *meta*-substituted nitrobenzenes, chlorobenzenes, and anilines has been reported.[26] A linear plot is obtained for dipole moment of 4-substituted pyridines and pyridine 1-oxides against σ-value; this is not the case for 3-substituents,

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[22] Cumper, *Chem. and Ind.*, 1958, 1628.

[23] Katritzky, *Quart. Rev.*, 1959, **13**, 353.

[24] Cumper, Vogel, and Walker, *J.*, 1956, 3621.

[25] Rao, *Chem. and Ind.*, 1956, 666; Whetsel, Roberson, and Krell, *Analyt. Chem.*, 1958, **30**, 1598; Rao, Wahl, and Williams, *Canad. J. Chem.*, 1957, **35**, 1575.

[26] van Beek, *Rec. Trav. chim.*, 1957, **76**, 729.

TABLE 4.

Calculated differences in moments (D), C–X minus C–H.

3-Subst.	Benzene	Pyridine[a]	Nitrobenzene[b]	Pyridine 1-oxide[d]
Me	+0·37	+0·35	+0·37	+0·27
Cl	−1·58	−1·73	−(1·71, 1·53)	−1·43
Br	−1·56	−1·64	−(1·71, 1·53)[c]	−1·43
I	−1·40	−1·35	−(1·16, 1·02)[c]	−1·00
4-Subst.				
Me	+0·37	+0·39	+0·41	+0·31
Bu^t	+0·45	+0·52	+0·60	+0·44
Cl	−1·58	−1·43	−1·39	−1·36
Br	−1·56	−1·44	−1·35	−1·29
I	−1·40	—	−1·11	—
Ph	0	+0·34	+0·35	+0·42

[a] Calc. by assuming μ(pyridine) = 2·21 D.[21] [b] Calculated for 4-substituted compounds by assuming $\mu(NO_2)$ = 4·01 D.[20] [c] Using 4·01 D for $\mu(NO_2)$ gives complex values for halogen substituents. Values shown were arrived at by assuming μ(CMe) = 0·37 D (Cumper, Vogel, and Walker, *J.*, 1957, 3640) in 3-nitrotoluene (μ = 4·14 or 4·17 D) (ref. *b*, p. 4526), giving $\mu(NO_2)$ = 3·94 and 3·96 D, respectively. This illustrates the large possible error for 3-substituted compounds. [d] Calc. by assuming μ(pyridine oxide) = 4·19 D.

where the actual dipole moment acts at an angle to the direction of the electronic displacements, depending on the relative magnitudes of the substituent moments, and may not reflect in a simple manner the degree of interaction between the groups. If C–X *minus* C–H moments of both 3- and 4-substituents are plotted against σ values[27] (see Figs. 1, 2, and 3) a good approach to linearity is obtained.

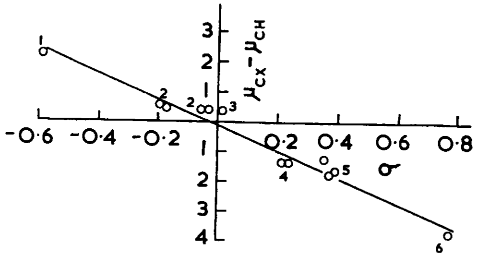

Fig. 1, Pyridines.

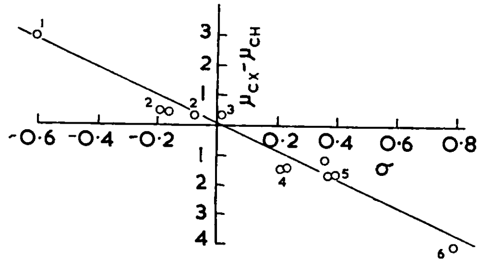

Fig. 2, Nitrobenzenes.

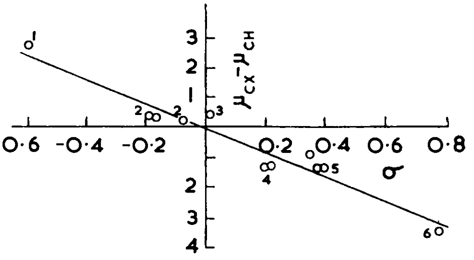

Fig. 3, Pyridine 1-oxides.

FIGS. 1—3. Differences in calculated moments, C–X minus C–H, plotted against σ-values.

1, 4-NMe$_2$. 2, 3- and 4-Alkyl. 3, 4-Ph. 4, 4-Hal. 5, 3-Hal. 6, 4-NO$_2$.

Plots of extinction coefficient and stretching frequency[28] against σ value for the N–O group in substituted pyridine 1-oxides show good linearity, and deviations by the methylamino-, dimethylamino-, cyano-, and nitro-groups indicate electron drift towards the ring relative to that in benzene.

The integrated absorption intensity of the N–O in-plane bending vibration should

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[27] Jaffé, *Chem. Rev.*, 1953, **53**, 191.

[28] Katritzky and Gardner, *J.*, 1958, 2192.

be a function of the dipole moment of the group and hence of the mesomeric moment of this group with the remainder of the molecule. Katritzky [23] suggests that the bands occurring at about 850 cm.$^{-1}$ may be due to this vibrational mode. A plot of the maximum extinction coefficients of these bands against mesomeric moment (as calculated by Katritzky, Randall, and Sutton [3]) is shown in Fig. 4. It is surprising that, as the electron-releasing power of the substituent group is diminished, the extinction coefficient is increased.

On numerous occasions dipole moments have been used to indicate the importance of hyperconjugation in molecules.[29] One current view is that hyperconjugation is unimportant,[30] except perhaps in electronically excited or ionic species. Electron affinity increases significantly in the series, benzene < pyridine < nitrobenzene < pyridine 1-oxide, and important contributions from hyperconjugation in the alkyl derivatives might show up in marked differences in the moments of the methyl and the t-butyl group under the different electronic conditions. Further, if the capacity for hyperconjugation is greater for the methyl than for the t-butyl group, then the difference between the methyl and the t-butyl group moments should be smaller in pyridine 1-oxide than in benzene. The dipole moments are considered to be reliable since a homologous series was measured in each case. The differences (corrected for electrostatic induction) are: benzene 0·08, pyridine 1-oxide 0·05, pyridine 0·08 D. The similarity of these differences suggests that hyperconjugation is not important in determining the overall dipole moment of a molecule. An alternative but less likely explanation would be that hyperconjugation is of comparable importance for both the methyl and the t-butyl group.

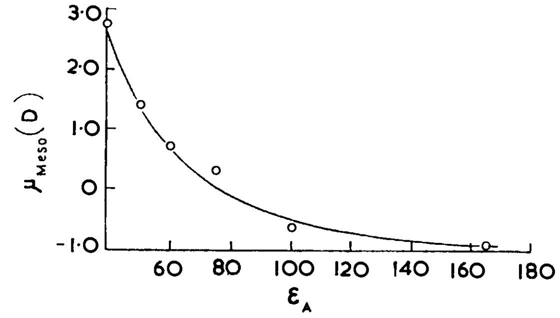

FIG. 4. Plot of mesomeric moment against extinction coefficient for the 850 cm.$^{-1}$ bands of pyridine 1-oxides. The points in order of decreasing μ_{MeSO} values for the four substituents are NMe_2, OMe, Me, COMe, and NO_2.

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[29] See under " Hyperconjugation " in ref. 20.

[30] Dewar and Schmeising, *Tetrahedron*, 1959, **5**, 166; Brown, *J. Amer. Chem. Soc.*, 1959, **81**, 3232.