THE USE OF DIPOLE MOMENTS IN THE CONFORMATIONAL ANALYSIS OF NICOTINIC ACID DERIVATIVES

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Apparent dipole moments in benzene of the compounds *II*–*VII*, together with the theoretical moments of their CNDO/2 models, can be employed in a semiquantitative estimate of conformational population in methyl nicotinate (*II*) and nicotinamide (*III*). In the case of nicotinic acid (*I*) this approach does not lead to unequivocal conclusions.

Nicotinic acid (*I*), its methyl ester (*II*) and amide (*III*) can exist in solutions as sets of rotamers. The situation can be characterized as an equilibrium between planar conformers with a limiting orientation of the functional groups, *i.e.* *Ia* ⇄ *Ib*, *IIa* ⇄ *IIb* or *IIIa* ⇄ *IIIb*. On the basis of this assumption Purcell[1,2] interpreted the dipole moment of the amide *III* (μ = 3·07 D) as a result of a mixture of 75% of the planar rotamer *IIIa* and 25% of the planar rotamer *IIIb*, whereas other authors[3–5], reporting dipole moments of the compounds *I*–*III* to be within the range 2·22–4·20 D, did not discuss these aspects. Semiempirical LCAO-MO calculations of the conformations of *I*–*III* show[6–11] that energetically most advantageous forms are not the planar rotamers *Ia*–*IIIa* or *Ib*–*IIIb* but more or less twisted molecules in which the heterocyclic ring and the functional group are not coplanar. The objective of this study was to investigate to what extent dipole moments[1–5] can be used for conformational study of the compounds *I*–*III* in solution. We repeated therefore the measurements of dipole moments[1–4] and studied also the model derivatives *IV*–*VII*, in which the orientation of the functional group relative to the heterocyclic ring is fixed by a five-membered lactone or lactam ring.

The compounds *IV*, *V* and *VII* were obtained according to the known procedures[12–14]. In order to prepare the hitherto unknown lactone *VI*, the anhydride *VIII* was reduced with lithium aluminium hydride to a mixture of two lactones (*VI* and *IX*). For structural assignment, an independent synthesis of one of these lactones was necessary and we synthesized therefore the lactone *VI* in the following way. 4-Methyl-3-cyanopyridine (*X*) was treated with bromosuccinimide, affording

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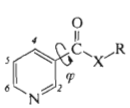
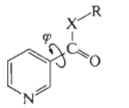
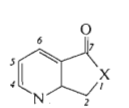
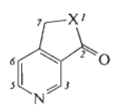
the dibromo derivative *XII* as the sole product. Analogously, methyl 4-methylnicotinate (*XI*) afforded the compound *XIII* under the same conditions. The derivative *XII* was easily transformed into the cyclic imino ether *XV* by alcoholysis in the presence of silver nitrate. Acid hydrolysis of this compound, followed by reduction of the reaction mixture with potassium borohydride, afforded the lactone *VI*, which was identical with the lactone m.p. 146–147°C, obtained by reduction of the anhydride *VII*.





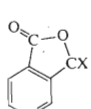


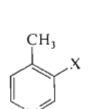


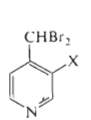
Ia–*IIIa* ($\varphi \rightarrow 0°$) *Ia*–*IIIa* ($\varphi \rightarrow 180°$)
I, X = O, R = H
II, X = O, R = CH_3
III, X = NH, R = H

IV, X = O
V, X = NH

VI, X = O
VII, H = NH



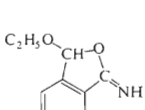


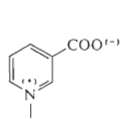


VIII, X = O
IX, X = H_2

X, X = CN
XI, X = CO_2CH_3

XII, X = CN
XIII, X = CO_2CH_3
XIV, X = $CONH_2$





XV *XVI*

EXPERIMENTAL

The temperature data are uncorrected. The melting points were determined on a Boetius hot stage microscope. The chromatographic separations were performed on alumina (activity II, Brockmann), the spots were detected by iodine vapours. ^{1}H-NMR spectra were taken at 37°C on a Varian XL-100 instrument with tetramethylsilane as internal standard; mass spectra were

measured on an LKB 9000 mass spectrometer and IR spectra on a Perkin Elmer 625 spectrophotometer.

Materials

Nicotinic acid (*I*), m.p. 231–232°C, and nicotinamide (*III*), m.p. 129–130°C were commercial products and were purified by crystallisation. Methyl nicotinate (*II*) was obtained by esterification[15] of the acid *I* and distillation of the crude product at 99–101°C/13 Torr; m.p. 38–40°C (ref.[15] reports m.p. 38°C).

6-Oxo-7*H*-furo[2,3-*b*]pyridine (*IV*)

This compound was prepared in 32% yield by reduction of 2,3-pyridinecarboximide with zinc and sodium hydroxide in the presence of copper sulphate[12]; m.p. 144–145°C (acetone). Ref.[12] reports m.p. 139–140°C. ^{1}H-NMR spectrum ($CDCl_3$, δ): 8·90 (q, H^4), 8·22 (dd, H^6), 7·51 (q, H^5), 5·35 (s, H^2). Mass spectrum, *m/e* (relative intensity, %): 135 (61), 134 (44), 106 (100), 105 (17), 78 (49), 77 (32), 51 (25), 50 (21); IR spectrum ($CHCl_3$): 1773 cm^{-1} ν(C=O), 1608 and 1590 cm^{-1} ν(CC and CN arom.), 2940 and 2860 cm^{-1} $\nu(CH_2)_{as,s}$.

6-Oxo-7*H*-pyrrolo[2,3-*b*]pyridine (*V*)

The compound *V* was obtained by the action of aqueous ammonia on ethyl 2-bromomethyl--3-pyridinecarboxylate hydrochloride[13]; needles melting at 207–208°C (ref.[13] states 204–206°C). ^{1}H-NMR spectrum ($CDCl_3$, δ): 8·78 (q, H^4), 8·17 (q, H^6), 7·60 (broad, s, H^1), 7·43 (q, H^5), 4·57 (s, H^2). Mass spectrum, *m/e* (relative intensity, %): 134 (100), 133 (28), 106 (33), 105 (16), 78 (30), 77 (20), 51 (18), 50 (16). IR spectrum ($CHCl_3$): 3450 and 3200 cm^{-1} $\nu(NH)_{free,assoc}$, 2925 and 2860 cm^{-1} $\nu(CH_2)_{as,s}$, 1720 cm^{-1} ν(C=O), 1610 and 1585 cm^{-1} ν(CC and CN arom.) or δ(NH).

2-Oxo-7*H*-furo[3,4-*c*]pyridine (*VI*)

A) A solution of 3,4-pyridinedicarbanhydride[16] (*VIII*) (2·0 g) in ether (100 ml) was added dropwise under stirring and cooling (−25°C) in the course of 30 min to lithium aluminium hydride (350 mg) in ether (80 ml). During another 30 min the temperature was allowed to rise to 0°C, the mixture was kept at his temperature for 2 hours and then decomposed with sodium hydroxide solution. The insoluble portion was filtered, dissolved in conc. hydrochloric acid (15 ml) and the solution refluxed for 2 hours. The mixture was taken down, the residue made alkaline (pH 8–9) by addition of saturated sodium hydrogen carbonate solution and solid potassium carbonate. The product was taken up in chloroform (total 200 ml) and the extract dried over sodium sulphate. After evaporation of the solvent *in vacuo* the residue was sublimed at 90°C/0·5 Torr, affording 750 mg (41%) of crystals, m.p. 103–135°C. According to ^{1}H-NMR spectrum, the product was a 3 : 1 mixture of isomeric lactones *VI* and *IX*. ^{1}H-NMR signals of the lactone *VI* ($CDCl_3$, δ): 9·18 (s, H^2), ~8·9 (d, H^5), 7·59 (d, H^6), 5·4 (s, H^7); signals of the lactone *IX*: 9·01 (d, H^5), ~8·9 (d, H^5), 7·82 (d, H^6), 5·5 (s, H^3). The crystalline mixture was subjected to fractional sublimation at 40°C, 60°C and 90°C at 0·5 Torr. The third portion melted at 146–147°C and on crystallisation from benzene afforded the lactone *VI*, m.p. 147–148°C. Its ^{1}H-NMR spectrum did not exhibit signals of the isomer *IX*. Mass spectrum, *m/e* (relative intensity, %): 135 (100), 134 (21), 106 (76), 105 (11), 78 (60), 77 (16), 51 (33), 50 (36). IR spectrum ($CHCl_3$): 2950 and 2840 cm^{-1} $\nu(CH_2)_{as,s}$, 1778 cm^{-1} ν(C=O), 1610 and 1590 cm^{-1} ν(CC and CN arom.). For $C_7H_5NO_2$ (135·1) calculated: 62·22% C, 3·73% H, 10·37% N; found: 61·96% C, 4·04% H, 10·57% N.

B) Dilute (1 : 2) hydrochloric acid (15 ml) was poured on compound *XV* (1 g), the mixture was refluxed for 2 hours and taken down *in vacuo*. The residue was made alkaline by addition of saturated solution of sodium hydrogen carbonate (with cooling), potassium borohydride (303 mg) was added and the mixture was set aside for 12 hours at room temperature. After addition of dilute (1 : 1) hydrochloric acid (2 ml) the solution was evaporated *in vacuo* and the residue repeatedly triturated with methanol (total amount 150 ml). The extract was taken down, the residue heated for 2 hours with concentrated hydrochloric acid (15 ml), evaporated and the residue made alkaline by addition of potassium hydrogen carbonate (pH 8—9). The product was taken up in chloroform (total volume 200 ml), the extract dried over sodium sulphate and the solvent evaporated. Sublimation of the residue at 90°C/0·5 Torr afforded 120 mg (16%) of the lactone *VI*, m.p. 146—147°C, which had spectral characteristics identical with those of the sample obtained by the procedure *A*).

2-Oxo-7*H*-pyrrolo[3,4-*c*]pyridine (*VII*)

Prepared by treatment of 3,4-pyridinecarboxamide[14] with tin and hydrochloric acid; needles, m.p. 199—200°C. ^{1}H-NMR spectrum ($CDCl_3$, δ): 9·15 (s, H^3), 8·80 (d, H^5), 7·70 (broad s, H^1), 7·48 (d, H^6), 4·54 (s, H^7). Mass spectrum, *m/e* (relative intensity, %): 134 (100), 133 (24), 106 (23), 105 (21), 78 (26), 77 (9), 51 (14), 50 (16). IR spectrum ($CHCl_3$, cm^{-1}): 3458 and 3180 ν(free and bonded NH), 2914 and 2860 $\nu(CH_2)_{s,as}$, 1710 ν(C=O), 1680, 1613 and 1515 ν(CC and CN arom.) or δ(NH).

4-Dibromomethyl-3-cyanopyridine (*XII*)

N-Bromosuccinimide (36 g) and dibenzoyl peroxide (1 g) were added to a solution of 4-methyl-3-cyanopyridine[17] (*X*) (10 g) in tetrachloromethane (350 ml) and the mixture was refluxed for 8 hours till the solution became colourless. The separated succinimide and insoluble material were filtered the filtrate taken down and the residue was crystallized from ethanol, yielding 12 g (51%) of yellowish crystals of *XII*, m.p. 94—96°C, ^{1}H-NMR spectrum (CD_3OD, δ): 8·90 (d, H^6), 8·95 (s, H^2), 7·95 (d, H^5), 7·23 (s, H—CBr_2); all the signals had equal intensity.

4-Dibromomethyl-3-methoxycarbonylpyridine (*XIII*)

4-Methyl-3-ethoxycarbonylpyridine[18] (*XI*) (10 g) was treated with N-bromosuccinimide (15 g) and dibenzoyl peroxide (1 g) in tetrachloromethane as described in the preceding experiment. After 5 hours the reaction mixture contained (according to thin-layer chromatography, benzene–chloroform 3 : 2) two products (R_F 0·41 and 0·56) together with the unreacted ester *XI* (R_F 0·30). Another amount of bromosuccinimide (15 g) and dibenzoyl peroxide (1 g) was added and after 3 hours the mixture contained only one compound, R_F 0·56. The insoluble material was filtered off and dry hydrogen chloride was introduced into the filtrate. The separated hydrochloride of the compound *XIII* was obtained as a yellow powder, m.p. 106—110°C (decomposition). ^{1}H-NMR spectrum (CD_3OD, δ): 9·37 (s, H^2), 9·16 (d, H^6), 8·76 (d, H^5), 8·04 (s, H—CBr_2), 4·02 (s, CH_3O); ratio of intensities of the respective signals 1 : 1 : 1 : 1 : 3. The free base *XIII* was unstable and was therefore transformed into the corresponding amide. The hydrochloride of *XIII* (1 g) was dissolved in methanolic ammonia (130 mg NH_3/1 ml; 30 ml), allowed to stand overnight at room temperature and taken down. The residue was washed with water and crystallised from methanol, yielding 450 mg of 4-dibromomethyl-3-pyridinecarboxamide (*XIV*), m.p. 134—136°C. ^{1}H-NMR spectrum (hexadeuteriodimethylsulphoxide, δ): 8·78 (s, H^2), 8·72 (d, H^6),

8·48 (broad s, NH), 7·90 (d, H^5), 7·84 (broad s, NH), 7·62 (s, H—CBr_2); all signals exhibited equal intensities. Mass spectrum contained molecular peak, *m/e* 325, in accord with the formula $C_7H_6Br_2N_2O$, together with the isotope peaks *m/e* 323 and 321.

7-Ethoxy-2-imino-7*H*-furo[3,4-*c*]pyridine (*XV*)

A solution of silver nitrate (30·3 g) in water (20 ml) was added to a boiling solution of the dibromo derivative *XII* (15·5 g) in 96% ethanol (100 ml) and the mixture was heated for 4 hours. The silver ions were removed by addition of excess concentrated hydrochloric acid and filtration of the precipitate. The filtrate was evaporated *in vacuo* and made alkaline (pH 8—9) by addition of potassium hydrogen carbonate and potassium carbonate. The separated product was taken up in chloroform (total 350 ml), the chloroform extracts were dried over magnesium sulphate and taken down, leaving 7·1 g (71%) of *XV* which was crystallised from acetone–benzene (1 : 1); m.p. 132—133°C. ^{1}H-NMR spectrum ($CDCl_3$, δ): 9·08 (s, H^2), 8·87 (d, H^5), 8·52 (broad s, NH), 7·57 (d, H^6), 6·00 (s, H^7), 4·64 (q, CH_2), 1·25 (t, CH_3). Mass spectrum, *m/e* (relative intensity, %): 178 (3), 163 (8), 149 (2), 133 (100), 106 (4), 105 (10), 78 (16), 77 (4), 51 (12), 50 (9). IR spectrum ($CHCl_3$): 3440 and 3210 cm^{-1} ν(free and bonded NH), 2980, 2930, 2880 and 2850 cm^{-1} $\nu(CH_3, CH_2)_{s,as}$, 1718 cm^{-1} ν(C=N), 1610 cm^{-1} ν(CC and CN arom. or δ(NH)).

Dipole Moments

The measurements were carried out in dilute benzene and dioxane solutions of compounds *I*— *VII*. The permittivity was measured at 1·2 MHz and 25°C, the density at 25°C. The measurements were evaluated using the method of Halverstadt and Kumler[19]. The mean uncertainty in the calculated moments was ±0·05 D. The data in Table I are given under assumption that $P_A = 5\% P_E$. The quantum chemical calculation of the dipole moment μ was based on CNDO/2 electron distribution in the compounds[10,11] *I*—*III* and on an analogous calculation for the bicyclic compounds *IV*— *VII* (for the vector addition both heterocyclic rings were assumed to be equilateral) according to the relationship[20]

$$\mu = [\sum_{i=x,y,z} [\mu_i^n + \mu_i^h)^2]^{1/2} ,$$

where μ_i^n and μ_i^h are the corresponding charge and hybridisation components of the moment. For the expression in terms of electron distribution see ref.[20]. The vector addition of the bond dipole moments for the planar molecules of *I*— *VII* was carried out graphically using the values of partial moments (see p. 33 in ref.[21]) under the additional assumption that $\mu(C_{a1}—N) \approx \approx \mu(C(=O)—N) = 0·45$D.

RESULTS AND DISCUSSION

It was already shown[21,22] that the value of dipole moments, calculated from the dielectric constants of solutions, can be used for the conformational studies only if the contribution of the solvent effect can be eliminated or determined and, moreover, if suitable models with sufficiently accurately defined dipole moments are available.

From the results summarised in Table I three main conclusions can be drawn: *1*) The "dioxane effect"[21] in the studied series of compounds *I*—*VII* is inconsistent

in respect of the magnitude and unfortunately also of the direction ($\Delta\mu = \mu(C_6H_6) - \mu$ (dioxane) = $-1{\cdot}01$ to $+0{\cdot}40$ D). A direct interpretation of this effect in relation to the structure of compounds *I–VII* is therefore imposible. 2) The vector addition method and the CNDO/2 approach lead only to an analogous sequence of theoretical values of μ for the rotamers of compounds *I–III* and for the pairs of 2- or 4-isomers of the model compounds *IV–VII*. In most cases, however, the absolute values μ for both the approaches differ by more than 0·5 D, so that there is no roughly equivalent series of theoretical data. 3) In the case of conformationally fixed compounds *IV–VII* it is obvious that on transition from dioxane to benzene the found value of μ comes closer to the value obtained by the CNDO/2 calculations. From this point of view the quantum chemical calculation of the compounds *I–VII* appears to be more perfect than a simple vector addition.

The difference between the dipole moments found for the compounds *IV–VI* and the corresponding values calculated by the CNDO/2 approach ranges between 0·09 to 0·16 D (Table I) and there is no reason to assume that this difference should be substantially greater for the conformationally mobile derivatives *I–III*. In accord with this assumption, the values of μ, found for *II* and *III* in benzene, lie between the extreme CNDO/2 values which are lowest for the torsion angle $\varphi = 0°$

TABLE I

Dipole Moments, μ (D), of the Studied Compounds

Method[a]	Acid *I*	Ester *II*	2-Lactone *IV*	4-Lactone *VI*	Amide *III*	2-Lactam *V*	4-Lactam *VII*
Halverstadt–Kumler (dioxane, 25°C)	2·77[b]	3·20	2·96	4·08	3·43	3·10	3·74
Halverstadt–Kumler (benzene, 25°C)	[c]	2·43[d]	3·19	4·48	3·37[e]	2·09	[c]
CNDO/2 method	1·03[f] 2·77	1·00[f] 2·70	3·32	4·57	1·70[f] 5·33	1·83	5·03
Vector addition	1·52[f] 3·44	0·14[f] 3·12	2·24	3·96	1·64[f] 3·80	1·42	4·36
Vector addition[g]	1·74[f] 3·84	0·49[f] 3·42	2·14	3·76	1·80[f] 4·18	1·02	4·66

[a] See Experimental; [b] ref.[3] reports 2·65 D; [c] values not reproducible due to low solubility; [d] ref.[4] reports 2·22 D; [e] refs[1,2] state 3·07 ± 0·04 D; [f] first value for $\varphi = 0°$, second value for $\varphi = 180°$; [g] the effect of the heteroaromatic nucleus was approximated by using the approximate dipole moment for pyridine (2·1 D).

and highest for $\varphi = 180°$ (see Fig. 1). From this fact we can conclude that in benzene the compounds *II* and *III* do not exist as single rotamers of the type *IIa* (*IIIa*) or *IIb* (*IIIb*). If we consider two conformations, corresponding to two minima $\varphi_1 = 10°$ (33°) and $\varphi_2 = 160°$ (117°) on the EHT plots[7,11] of total electron energy against the torsion angle φ, the relative population of both conformers can be assessed semiquantitatively (see p. 49 in ref.[21]) using the equation

$$\mu^2(C_6H_6) = x\mu_1^2 + y\mu_2^2 , \qquad (1)$$

where μ_1 and μ_2 are dipole moments of compound *II* (or *III*) calculated by the CNDO/2 approach for the respective angles φ_1 and φ_2 which are taken from the graphs on Fig. 1, and x and y are weight fractions of the conformers of the type *IIa* (*IIIa*) and *IIb* (*IIIb*), respectively. From the data in Table I it follows that the ester *II* contains 22% of the conformer *IIa*, and the amide *III* 65% of the analogous conformer *IIIa*. Naturally, these data depend considerably on the accuracy of the experimental dipole moment determination: *e.g.* using the previously published values[1,2,4] which are lower only for 0·2 D, the calculation according to the relationship (*1*) leads to considerably different values: 38% and 76%, respectively. Application of this approach to the acid *I* is not suitable since the dipole moment can be measured

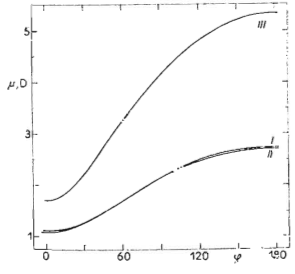


FIG. 1

Dependence of Dipole Moments of Nicotinic Acid (*I*), Methyl Nicotinate (*II*) and Nicotinamide (*III*), as Calculated by the CNDO/2 Method, on the Torsion Angle, φ, between the Planes of the Heteroaromatic Ring and the Functional Group

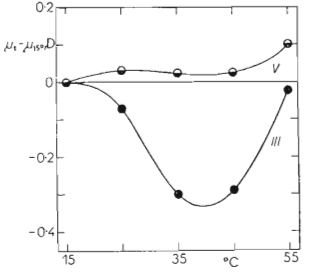


FIG. 2

Temperature Dependence of Apparent Dipole Moments of Nicotinamide (*III*) and the Lactam *V* in Benzene

only in dioxane and therefore its value depends on the uncertain correction due to the above-mentioned effect of this solvent. Moreover, some zwitterion *XVI* can exist in a polar medium; this species has undoubtedly an extremely high dipole moment (*e.g.* CNDO/2 calculation for $\varphi \approx 90°$ leads to $\mu = 16{\cdot}6$ D). Assuming that this ionisation does not take place, the relatively high value $\mu = 2{\cdot}77$ D would indicate that under the conditions of the measurement the acid *I* does not exist exclusively in one conformation (*Ia*) as found for the crystalline state[23].

We tried to support our conclusion concerning the conformational heterogeneity of the compounds *I*–*III* by investigation of the temperature dependence of μ for the amide *III* and the lactam *V*. As expected, the dipole moment for the geometrically fixed derivative *V* is constant within the range 15°C to 55°C (Fig. 2). On the contrary, the dipole moment for the conformationally mobile amide *III* decreases in the range 25°C–45°C whereas at higher temperatures it increases. This interesting course of the experimental dependence $\mu = f(T)$ can hardly be interpreted only in terms of different population of rotamers of the type *IIIa* or *IIIb* and it can be caused partly also by other factors which affect the temperature dependence of the apparent dipole moment.

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