Tautomerism of Heteroaromatic Compounds with Five-Membered Rings. 14.[1] Confirmation of the Structure of Reissert Salts as Condensed 5-Aminooxazolium Cations

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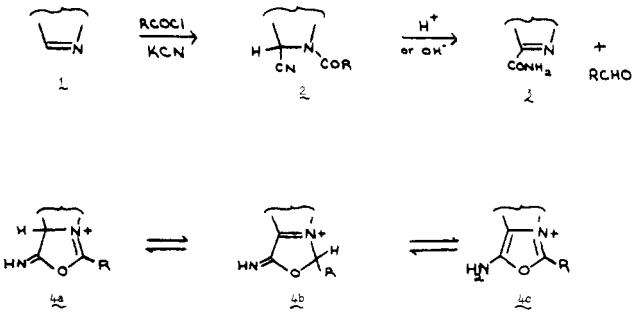
Abstract: Reissert salts exist in 5-aminooxazolium structures of type **4c** as is proved by a combination of NMR, deuterium exchange, and mass spectrometry techniques for seven representative examples. Previous evidence[9] that five of these salts existed predominantly in other tautomeric forms has been shown to be incorrect. An apparent major anomaly in the rationalization of the tautomeric structure of heteroaromatics is thus removed.

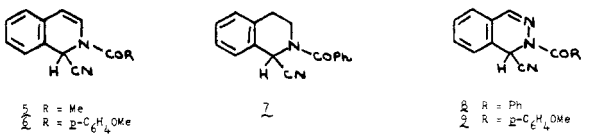
Many heteroaromatic compounds containing the structure element **1,** usually as part of a bi- or polycyclic system, on treatment with an acid chloride in the presence of KCN yield addition products **2,** known as Reissert compounds.[2] Hydrolysis of Reissert compounds, by either acid or base, usually leads to formation of the heterocyclocarboxyamide **3** and the aldehyde derived from the original acid chloride, a process of synthetic significance.[3]

The accepted mechanism for the acid-catalyzed hydrolysis of Reissert compounds was proposed by McEwen and Cobb[4] and involves protonation at the nitrile nitrogen followed by cyclization to **4a,** tautomeric conversion of this cation to **4b,** and subsequent hydrolysis to **3**. Reissert cations, considered to be intermediates in the acid-catalyzed hydrolysis, were later isolated as bromide[5] and tetrafluoroborate[6] and assigned structures of type **4a**. Whereas the McEwen mechanism for the acid-catalyzed hydrolysis of Reissert compounds, including the formation of cations of type **4a** and **4b** as transient intermediates, is reasonable, the possibility that cations of structural type **4a** had been isolated seemed unlikely. Structures **4a** and **4b** represent two out of three possible tautomeric forms of a



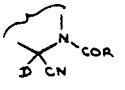
5-aminooxazolium cation: the tautomeric structures of aminoazolium cations have been extensively investigated[7] and amino structures of the third type **4c** were found to greatly predominate at equilibrium.[16] For monocyclic 5-aminooxazolium cations, the literature evidence is clearly compatible with such structures.[8] Moreover, for the Reissert cations, the experimental data of references 5 and 6 are not in disagreement with their formulation with structures of type **4c** and indeed the 1,3-dipolar additions reported by McEwen et al.[6] are more easily explained on such structures.

However, McEwen et al.[9] recently communicated the following surprising conclusions of their detailed investigation into the tautomeric structure of Reissert tetrafluoroborate salts: (i) The acetylisoquinolinium Reissert compound **5** with HBF_4–HOAc formed initially a cation of type **4a,** but on solution in $CDCl_3$–CF_3CO_2H it isomerized to at least 75% to the isomeric cation of type **4b,** which was isolated as the BF_4^- salt. (ii) The *p*-anisoyl analogue **6** formed a salt which in CF_3CO_2H solution was considered to exist 50% as form **4a** and/or **4b** [and 50% as **4c**]. (iii) The dihydroisoquinoline Reissert (**7**) and the two phthalazine Reissert compounds (**8, 9**) formed fluoroborates which in CF_3CO_2H had structures of type **4a**.



These findings, if confirmed, would constitute a major anomaly in the rationalization of heteroaromatic tautomerism,[7] and we therefore examined them carefully. We now present results which refute the foregoing conclusions, and which constitute conclusive evidence for structures of type **4c** for a variety of Reissert cations.

Deuteration Studies. For the three Reissert compounds **7–9** the finding that the fluoroborate salts were reconverted to the original Reissert compound on treatment with $NaHCO_3$–H_2O was quoted[9] as evidence for salt structure of type **4a,** the implication being hat the hydrogen α to the nitrogen in the original heterocycle remains in place. We find that treatment of these three Reissert salts, and also of that derived from **6,** with Na_2CO_3–H_2O does indeed give back the original Reissert compound, but that treatment with Na_2CO_3–D_2O gives the specifically α-deuterated Reissert compounds **10,** as shown by



the NMR spectra (Table I) and by the mass spectra (see later). This finding is clearly compatible with structures of type **4c** for the salts and gives no support to structures of type **4a**.

NMR Studies. The remaining published evidence[9] for the existence of the salts from **7–9** in forms of type **4a,** and of the salt from **6** to exist to an extent of only 50% in a form of type **4c** was derived from NMR spectra. In each case the signal for the controversial oxazolium ring 4-H characteristic of structure **4a** was considered to fall within the complex multiplets arising from the aromatic protons, and the claimed evidence for its presence came from integrations of spectra taken in CF_3CO_2H.

We have remeasured the NMR spectra of the CF_3CO_2H salts of **6–9** (Figures 1a, 2a, 3a, 4a) and find no evidence for

Table I. 60 MHz NMR Spectra of Reissert Compounds[a]

Compd		Chemical shifts (δ)
2-Acetyl-1,2-dihydroisoquinaldonitrile (**5**)	αH	2.27 (3 H, s), 6.12 (1 H, d, J = 8 Hz), 6.79 (2 H, m), 7.32 (4 H, m)
	αD	2.27 (3 H, s), 6.12 (1 H, d, J = 8 Hz), 6.79 (1 H, d, J = 8 Hz), 7.32 (4 H, m)
2-*p*-Anisoyl-1,2-dihydroisoquinaldonitrile (**6**)	αH	3.83 (3 H, s), 6.06 (1 H, d, J = 7 Hz), 6.49 (1 H, s), 6.70 (1 H, d, J = 7 Hz), 6.93 (2 H, d, J = 9 Hz), 7.32 (4 H, m), 7.60 (2 H, d, J = 9 Hz)
	αD	As above 6.49 (1 H, s) absent
2-Benzoyl-1,2,3,4-tetrahydroisoquinaldonitrile (**7**)	αH	2.80–4.20 (4 H, m), 6.33 (1 H, s), 7.32 (4 H, s), 7.52 (5 H, d)
	αD	As above 6.33 (1 H, s) absent
2-Benzoyl-1-cyano-1,2-dihydrophthalazine (**8**)	αH	7.4–8.0 (10 H, m)
	αD	7.4–8.0 (9 H, m)
2-*p*-Anisoyl-1-cyano-1,2-dihydrophthalazine (**9**)	αH	3.84 (3 H, s), 6.94 (3 H, m), 7.53 (4 H, s), 7.84 (2 H, d, J = 8 Hz)
	αD	3.84 (3 H, s), 6.94 (2 H, d, J = 8 Hz), 7.53 (4 H, s), 7.84 (2 H, d, J = 8 Hz)

[a] In $CDCl_3$ with Me_4Si as internal standard.

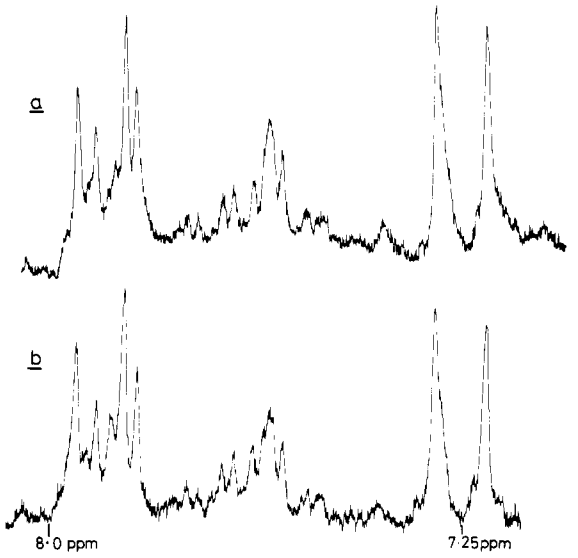


Figure 1. (a) The aromatic region of the 100 MHz spectrum of the Reissert salt of **6** obtained by dissolving **6** in trifluoroacetic acid. (b) The corresponding spectrum of a solution of the α-deuterated analog of **6** in trifluoroacetic acid-*d*.

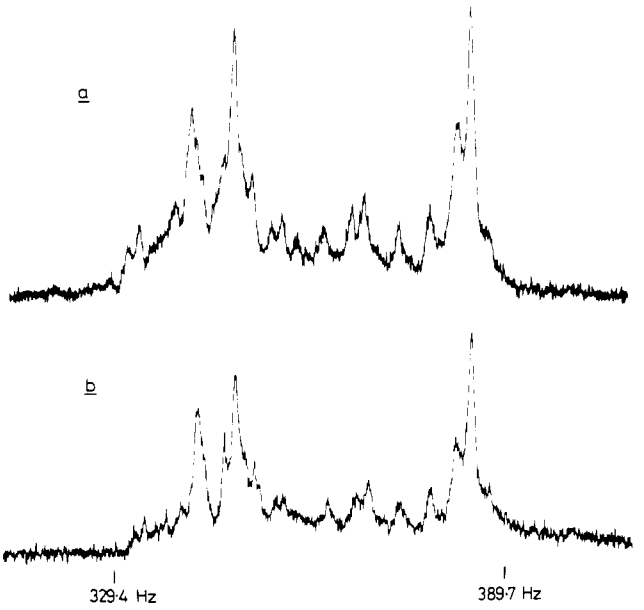


Figure 2. (a) The aromatic region of the 100 MHz spectrum of the Reissert salt of **7** obtained by dissolving **7** in trifluoroacetic acid. (b) The corresponding spectrum of a solution of the α-deuterated analog of **7** in trifluoroacetic acid-*d* (the calibration refers to Hz upfield from the trifluoroacetic acid proton used as a lock signal).

any signal for the CH of structure **4a** (or of **4b**); such a signal should appear as an unsplit singlet. Conclusive evidence for the absence of any significant quantity of tautomeric form of type **4a** or **4b** in the salt is provided by comparison of the CF_3CO_2H solution of the normal Reissert salts with CF_3CO_2D solutions of salts prepared from the specifically deuterated Reissert compounds (cf. **10**). If the salts from the deuterated compounds **10** exist in structures of type **4a,** the 4 position must be deuterated, as must the 2 position of structures of type **4b.** In each of the four cases detailed comparison of the NMR spectra (Figures 1a with 1b, etc.) shows no significant differences, proving the absence of detectable amounts of structures of type **4a** and **4b,** and thus demonstrating structure **4c**.

In our view, McEwen was misled into the erroneous structure for the cations from **6–9** by placing too much reliance on the accuracy of integrals for poorly resolved 60 MHz spectra.[17]

Experiments with the Acetylisoquinolinium Reissert Compound. McEwen reported[9] that the salt from **5** showed in $(CD_3)_2SO$ solution a 3-proton singlet at δ 2.88 (CH_3) and a 7-proton multiplet at δ 7.2–7.8 assigned to the six isoquinoline ring protons together with the oxazole 4-position C–H of structure type **4a.** Our spectra for this salt in $(CD_3)_2CO$ and $(CD_3)_2SO$ are shown in Figure 5. In the former solvent we assign the broad peak at δ 7.0 to the NH_2 group. For the solution in $(CD_3)_2SO$, we believe that the NH_2 signal absorbs in the aromatic region but is broadened to an extent that it is no longer recognizable. Indeed, integration of the methyl group signal against the aromatic region multiplet (by cutting out and weighing six separate traces) gave a ratio of 3:7.97 ± 0.13 (standard deviation). Our results suggest therefore that for both solvents **4c** is the predominant tautomer.

The claimed[9] isomerization of the HBF_4 salt of **5** from a structure of type **4a** to one of type **4b** was attempted repeatedly under the conditions reported. At no time could we detect any isomeric salt; a white sublimable solid was found in each case which was proved to be NH_4BF_4 by comparison with an authentic sample. Attempts to follow the alleged isomerization by NMR indicated that the original CH_3 singlet was initially converted to two doublets which finally disappeared to give a third doublet. Deep seated decomposition evidently occurs under these conditions.

Methoxy-Substituted Isoquinolinium Reissert Salts. To simplify the NMR spectra in the aromatic region, we have prepared methoxy-substituted Reissert compounds. 2,2-Dimethoxyethylamine and 3,5-dimethoxybenzaldehyde gave

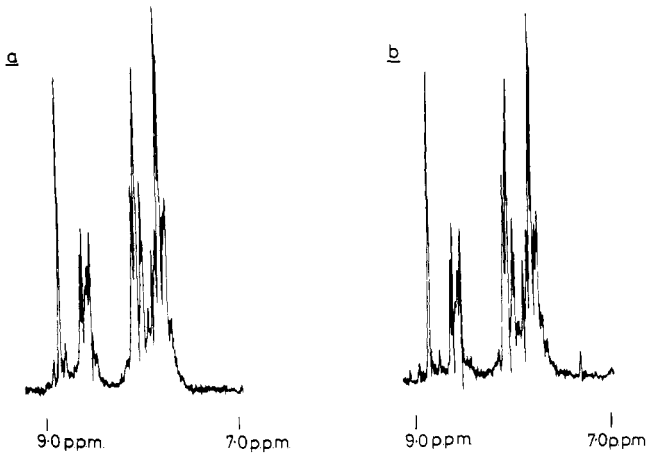
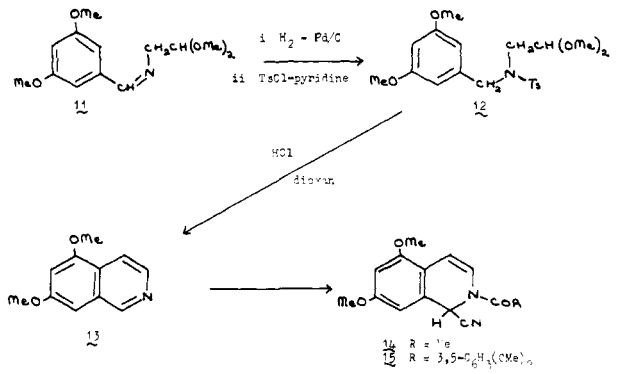


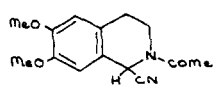
Figure 3. (a) The 100 MHz spectrum of the Reissert salt of **8** obtained by dissolving **8** in trifluoroacetic acid. (b) The corresponding spectrum of a solution of the α-deuterated analog of **8** in trifluoroacetic acid-*d*.

the imine **11**; attempted Pomeranz-Fritsch cyclization failed, but **11** was successively hydrogenated and tosylated to **12**, which, following the Jackson[10]-Bobbitt[11] method, we converted into the isoquinoline (**13**) and thus into the Reissert compounds (**14** and **15**). The fluoroborate salt derived from



14 was unstable, decomposing slowly in the solid at 0 °C and rapidly in solution; good NMR spectra were not obtained. The fluoroborate derived from **15** was more stable; the NMR spectrum obtained in $(CD_3)_2SO$ disclosed the expected two AB quartets and one A_2B multiplet in the aromatic region together with a broad 2-proton peak at 8.18 ppm, assigned to the NH_2 proton of tautomeric form of type **4c.** The peak at 8.18 ppm disappeared on the addition of a little CF_3CO_2H owing to rapid exchange (Table II). Again we conclude that the cation derived from **15** exists very predominantly in tautomeric form **4c**.

3,4-Dihydro-6,7-dimethoxyisoquinoline was converted into the Reissert compound **16.** The NMR spectrum of the salt derived from this compound (Table II), discussed in detail elsewhere,[12] is also compatible with a structure of type **4c.** In particular, the methyl singlet at 2.75 ppm precludes structure type **4b** and the broad singlet at 6.24, though integrating for 1.6 H rather than 2 H presumably because of partial H-D exchange with solvent, is best assigned to NH_2 protons.



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Mass Spectra of Reissert Compounds. The Reissert compounds **6–9** each gave a molecular ion in the low resolution mass spectrum and we utilized this property to confirm the

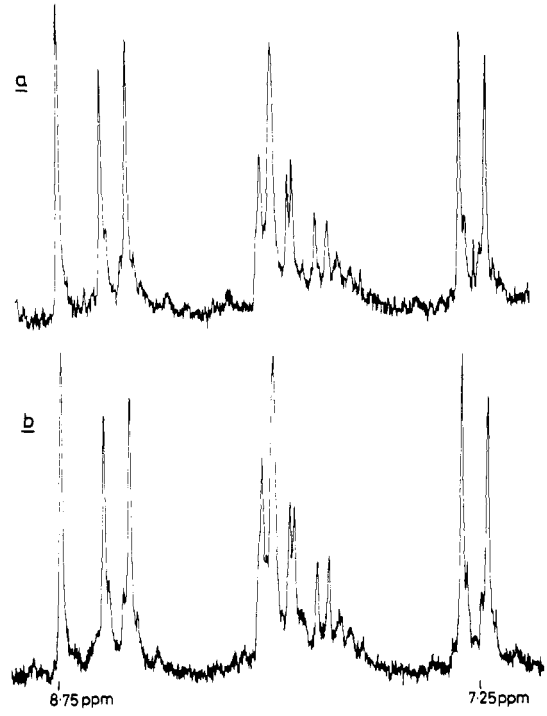

Figure 4. (a) The aromatic region of the 100 MHz spectrum of the Reissert salt of **9** obtained by dissolving **9** in trifluoroacetic acid. (b) The corresponding spectrum of the α-deuterated analog of **9** in trifluoroacetic acid-*d*.

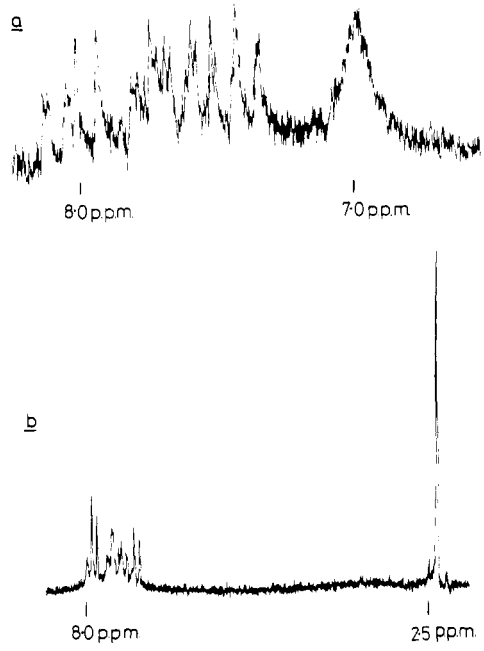

Figure 5. (a) The aromatic region of the 100 MHz spectrum of the fluoroborate salt of **5** in acetone-d_6. (b) The 100 MHz spectrum of the fluoroborate salt of **5** in dimethyl sulfoxide-d_6.

incorporation of a single deuterium atom in the α position in the exchange experiments discussed above. The mass spectral fragmentation of Reissert compounds having quinoline, isoquinoline, and phthalazine nuclei has been investigated by Popp et al.[13] Our spectra confirm their conclusion that there is initial loss of the N substituent. We also find that the next stage is loss of CN which competes with loss of HCN in **6** and **7**. In the former, loss of CN is the major pathway but both routes are important in **7**. In the phthalazine derivatives **8** and **9**, the loss of CN predominates over loss of N_2. Thus in **8**, *m/e*

Table II. 100 MHz NMR Spectra of Fluoroborate Salts of Reissert Compounds[a]

Compd	Chemical shifts (δ)
Salt of 2-(3,5-dimethoxybenzoyl)1,2-dihydro-5,7-dimethoxyisoquinaldonitrile[b]	3.93 (6 H, s), 4.02 (6 H, s), 6.76 (1 H, d, J = 2 Hz), 6.94 (1 H, d, J = 2 Hz), 7.1 (3 H, s), 7.47 (1 H, d, J = 8 Hz), 8.06 (1 H, d, J = 8 Hz), 8.18 (2 H, br)
Salt of 2-acetyl-1,2,3,4-tetrahydro-6,7-dimethoxyisoquinaldonitrile[c]	2.75 (3 H, s), 3.18 (2 H, t, J = 7 Hz), 3.82 (3 H, s), 3.84 (3 H, s), 4.44 (2 H, t, J = 7 Hz), 6.24[d] (br), 7.02 (1 H, s), 7.24 (1 H, s)

[a] Me_4Si as internal standard. [b] In $(CD_3)_2SO$. [c] In $(CD_3)_2CO$. [d] Undergoes slow exchange with solvent (see text).

Table III. Reissert Compounds and Derived Hydrofluoroborate Salts

Compd	Yield, %	Mp (lit. mp), °C	Mp of salt (lit. mp), °C
2-Acetyl-1,2-dihydroisoquinaldonitrile (**5**)	95	121–121.5 (119–120)[a]	169 (169–170)[b]
2-*p*-Anisoyl-1,2-dihydroisoquinaldonitrile (**6**)	80	175–176 (173–174)[c]	*d*
2-Benzoyl-1,2,3,4-tetrahydroisoquinaldonitrile (**7**)	40	123–124 (104–105)[e] (cf. 126–127)[f]	*d*
2-Benzoyl-1-cyano-1,2-dihydrophthalazine (**8**)	10	162–164 (163–164)[g]	*d*
2-*p*-Anisoyl-1-cyano-1,2-dihydrophthalazine (**9**)	54	172–174[h]	*d*
12-Acetyl-1,2-dihydro-5,7-dimethoxyisoquinaldonitrile (**14**)	38	175–194 dec[h]	140–142[h]
2-(3,5-Dimethoxybenzoyl)-1,2-dihydro-5,7-dimethoxyisoquinaldonitrile (**15**)	45	176–195 dec[h]	189[h]
2-Acetyl-1,2,3,4-tetrahydro-6,7-dimethoxyisoquinaldonitrile (**16**)	30	200[h]	175–176[h]

[a] F. D. Popp, W. Blount, and A. Soto, *Chem. Ind. (London)*, 1022 (1962). [b] Reference 9. [c] F. D. Popp and A. Soto, *J. Chem. Soc.*, 1760 (1963). [d] Reissert salt formed with CF_3CO_2H in situ, see text. [e] I. W. Elliott and J. O. Leflore, *J. Org. Chem.*, **28**, 3181 (1963). [f] I. C. Wang, Ph.D. Thesis, University of Massachusetts, 1971. [g] F. D. Popp, J. M. Wefer, and C. W. Klinowski, *J. Heterocycl. Chem.*, **5**, 879 (1968). [h] Compound not previously reported. Satisfactory elemental analysis was obtained.

130 is 12% of the base peak whereas *m/e* 128 is only 2%. This result differs somewhat from that obtained by Popp et al.[13] who found that the loss of N_2 was the major pathway in **8**.

General Conclusions. The tautomeric structure of Reissert salts is thus very predominantly that of 5-aminooxazolium cations. This is exactly as is expected from the general pattern of tautomeric behavior in heteroaromatic compounds;[7] amino compounds almost always exist as such and not in alternative imino forms.

Experimental Section

NMR spectra were obtained at 100 MHz using a Varian Associates HA 100 spectrometer operating at 38 °C and 60 MHz using a Perkin-Elmer R12 spectrometer. IR spectra were recorded using a Perkin-Elmer 257 spectrophotometer and low resolution mass spectra were obtained using a Hitachi Perkin-Elmer RMU-6E system.

Materials. Isoquinoline and phthalazine were obtained from commercial sources. 3,4-Dihydroisoquinoline, characterized as the *hydrochloride*, mp 165–167 °C (Anal. Calcd for $C_9H_{10}ClN$: C, 64.5; H, 6.0; N, 8.4. Found: C, 64.8; H, 6.1; N, 8.4), was prepared using the general route to this class of compound.[14] 3,4-Dihydro-6,7-dimethoxyisoquinoline,[15] bp 145 °C (1.5 mm) (lit.[15] 150–156 °C (2–3 mm)), was prepared by the literature method.[15] Yield and melting point data for Reissert compounds and derived hydrofluoroborate salts are given in Table III.

5,7-Dimethoxyisoquinoline. (a) ***N*-(2,2-Dimethoxyethyl)-3,5-dimethoxybenzylidenimine (11).** 2,2-Dimethoxyethylamine (0.76 g) was added to 3,5-dimethoxybenzaldehyde (1.0 g) dissolved in absolute ethanol (5 ml). After standing at 20 °C for 16 h the volatile material was removed at 90 °C (20 mm), and the residue was distilled to give the imine (1.3 g, 90%) as an oil, bp 120 °C (0.1 mm). IR (neat) 3040–2800, 1650, 1600, 1460, 1430, 1345, 1320, 1300, 1210, 1155, 1130, 1065, 965, 930, 850, 690 cm^{-1}; NMR (CCl_4) δ 8.15 (s, 1 H), 6.90 (d, 2 H), 6.49 (t, 1 H), 4.7 (t, 3 H), 3.87 (s, 6 H), 3.72 (d, 2 H), 3.40 (s, 6 H). Anal. Calcd for $C_{13}H_{19}NO_4$: C, 61.6; H, 7.6; N, 5.5. Found: C, 61.7; H, 7.4; N, 5.2.

(b) ***N*-(2,2-Dimethoxyethyl)-3,5-dimethoxybenzylamine.** *N*-(2,2-Dimethoxyethyl)-3,5-dimethoxybenzylidenimine (1.5 g) in Analar methanol (15 ml) was shaken under hydrogen at 20 °C (760 mm) with 5% palladium on charcoal (0.2 g). One mole of hydrogen was taken up in 20 min. The solution was filtered and distilled to give the amine (1.3 g, 90%) as an oil, bp 180 °C (1.3 mm). IR (neat) 3330, 3100–2800, 1600, 1460, 1430, 1355, 1320, 1295, 1200, 1170–1040, 970, 925, 840, 695 cm^{-1}; NMR (CCl_4) 6.45 (d, 2 H), 6.30 (t, 1 H), 4.38 (t, 1 H), 3.67 (s, 7 H), 3.23 (s, 6 H), 2.65 (d, 2 H), 1.50 (s, 2 H). Anal. Calcd for $C_{13}H_{21}NO_4$: C, 61.2; H, 8.3; N, 5.5. Found: C, 61.1; H, 8.2; N, 5.2.

(c) **5,7-Dimethoxyisoquinoline (13).** *N*-(2,2-Dimethoxyethyl)-3,5-dimethoxybenzylamine (14.6 g) was added dropwise to a solution of tosyl chloride (21 g) in pyridine (70 ml) at 0 °C, over a period of 1 h. The solution was allowed to warm to 20 °C, to stand for a further 23 h, and taken up in chloroform (100 ml) and washed with a saturated solution of sodium carbonate (4 × 30 ml). The chloroform solution was dried over anhydrous sodium carbonate and evaporated at 20 mm. The last traces of pyridine were removed by adding dry toluene (40 ml), removing the toluene at 20 mm, and repeating three times. The crude tosylate produced only one spot on TLC (silica plate eluted with ethyl acetate), R_f 0.5. The tosylate was taken up in dioxane (570 ml) and to this was added 6 N HCl (90 ml). The solution was refluxed for 3.5 h and the solvent was removed at 20 mm. The residue was taken up in ether (50 ml) and washed with a saturated solution of sodium carbonate (2 × 30 ml) and dried over anhydrous sodium sulfate and evaporated down at 20 mm. The residue was purified on a chromatography column (alumina type H, ethyl acetate) and then on a second column (alumina type H, chloroform). The crude isoquinoline obtained was taken up in ethanol (100 ml) and added to a saturated solution of HCl gas in ethanol (50 ml). The solution was evaporated down to 70 ml and left to cool.

5,7-Dimethoxyisoquinoline hydrochloride (6.2 g, 41%) was collected as yellow needles from *n*-propyl alcohol, mp 192–193 °C. IR (Nujol) 3000, 2400, 2100, 1620, 1460, 1360, 1330, 1210, 1120, 1165, 1125, 1035, 900, 850, 675 cm^{-1}; NMR (DMSO-d_6), 9.4 (1 H), 8.4 (2 H), 7.3 (1 H), 7.1 (1 H), 4.0 (6 H). Anal. Calcd for $C_{11}H_{12}ClNO_2$: C, 58.6; H, 5.4; N, 6.2. Found: C, 58.5; H, 5.5; N, 6.1.

Reissert Compounds and Their Hydrofluoroborate Salts. To a stirred mixture of the heterocyclic base (1.0 g) in CH_2Cl_2 (15 ml) and KCN (1.0 g) in water (5 ml) was added the acid chloride (2 equiv to 1 of base) in CH_2Cl_2 (5 ml) over 2 h. The resultant mixture was stirred for a further 6 h after which water (10 ml) and CH_2Cl_2 (15 ml) were added. The aqueous layer was extracted with CH_2Cl_2 (10 ml). The combined organic solutions were washed with water (20 ml), 1 N HCl (20 ml), 1 N NaOH (20 ml), and water (20 ml), dried ($MgSO_4$), reduced in volume to 10 ml, and decolorized with charcoal. Isopropyl

alcohol (ca. 10 ml) was added and evaporation and cooling caused precipitation of the Reissert compound. Treatment and of the Reissert compounds (x g) dissolved in a minimum of hot acetic acid, with 40% aqueous fluoroboric acid ($3.5 \times x$ g), followed by cooling produced the hydrofluoroborate salt which was collected by filtration and either washed or recrystallized from ethanol. Reissert compounds and their salts obtained via this general procedure are reported in Table III. New compounds gave satisfactory elemental analysis data and melting points of known compounds agreed with those reported previously.

α-Deuterated Reissert Compounds. These were prepared by the following general route. The Reissert compound (2 g) was taken up in sufficient TFA to obtain a clear solution (ca. 4 ml). This solution was added dropwise to a swirled flask containing dry ether (100 ml). The solid was filtered off and ground with anhydrous sodium carbonate in a mortar and pestle. D_2O (5–10 ml) was added to obtain a thick paste which was mixed thoroughly for 5 min. The mixture was then taken up in chloroform (20 ml), the organic layer separated, and the aqueous layer washed with chloroform (2×10 ml). The combined organic fractions were then dried (Na_2CO_3) and evaporated to dryness, and the product was recrystallized from 1:10 benzene/cyclohexane (ca. 20–40 ml). The α-deuterated Reissert compounds were shown to have melting points and mixed melting points identical with the parent compounds.

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References and Notes

(1) (a) Part XII: S. O. Chua, M. J. Cook, and A. R. Katritzky, *J. Chem. Soc. B*, 2350 (1971); (b) part XIII: G. Bianchi, A. J. Boulton, I. J. Fletcher, and A. R. Katritzky, *ibid.*, 2355 (1971).
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Kinetics and Thermodynamics of Intermolecular Saturated Amine Excimers

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Abstract: The rate constants and activation parameters pertaining to excimer formation in 1-azabicyclo[2.2.2]octane (ABCO) and 1-azaadamantane (1-AA) have been measured in n-hexane solution utilizing fluorescence decay data. These excimers are characterized spectroscopically by broad, very red-shifted emission bands (λ_{max} 375 and 395 nm, respectively). The formation rate constants are diffusion controlled and have been analyzed without the need to consider the "transient term". These excimers are rather tightly bound having ΔH values of −11.6 and −10.2 kcal/mol, respectively. In addition, the dissociation rate constant preexponential factors are typically large, with ΔS values of ca. 19 and 17 eu, respectively. The methodology of determining binding energies using the steady-state method vis-a-vis kinetic procedures is discussed; the former technique provides lower limits of $|\Delta H|$ values. For ABCO, the excimer relaxation rate constant, k_D, was found to be slightly temperature dependent ($W_D \sim 1.4$ kcal/mol), and an analysis of the temperature dependence of the excimer fluorescence quantum intensity revealed that it is the nonradiative portion of k_D which varies with temperature. The ABCO excimer is weakly quenched by ground-state amine ($k_{QD} = 7.2 \times 10^7$ M^{-1} s^{-1}). The photophysical properties of nonexcimer-forming amines are compared with ABCO and 1-AA, and an attempt is made to rationalize the stability of these excimers within simple exciton and charge resonance models. Neither approach appears to be adequate in accounting for the observed binding energies or in explaining the structural specificity in excimer formation in saturated amines. The structure of the excimer is discussed and configurations are proposed: head-to-head (N—N) and C–N bond antiparallel to C–N bond. The head-to-tail arrangement is excluded because 4-Me-ABCO also undergoes excimer formation and possesses similar thermodynamic properties. The photochemistry of ABCO and triethylamine (in n-hexane) solution is also discussed.

Introduction

The association between an electronically excited molecule and its ground-state counterpart (i.e., excimer formation) is a well-known phenomenon which has been extensively studied, both experimentally and theoretically, for about 20 years.[4-7] Until rather recently, however, investigations of organic molecular excimers and their formation, deactivation, stability, etc. have been confined to aromatic or heteroaromatic molecules.[7,8] Studies of excimer formation in some nonaromatic compounds, i.e., saturated tertiary amines, have been described recently.[9,10] It thus appears that the presence of the π-electronic system characteristic of aromatic molecules is not an essential criterion for the stabilization of excimers in organic molecules.[11] Thus the nonbonding electron pair in a saturated amine, when properly oriented in certain aliphatic systems can be very important in effecting excimer stabilization both *inter*molecularly and intramolecularly.[12] It is the purpose of this