Tetrahedron. Vol. 29, pp. 4153 to 4157. Pergamon Press 1973. Printed in Great Britain

ROTATION ABOUT THE EXOCYCLIC CARBON–CARBON DOUBLE BOND OF AMINO DIENES OF THE INDOLO[2,3-a]-AND BENZO[a]QUINOLIZIDINE SERIES

M. BÁRCZAI-BEKE, G. DÖRNYEI, G. TÓTH* and C. SZÁNTAY†
Institute of Organic Chemistry, Technical University of Budapest

(*Received in the UK* 29 *May* 1973; *Accepted for publication* 23 *July* 1973)

Summary—Quinolizidines containing an exocyclic double bond at C-2 (**1**, **2**) give on mild oxidation the amino dienes (**3**, **4**), as mixtures of geometric isomers with respect to the exocyclic double bond. The free enthalpy of activation for the rotation about the double bond has been estimated by NMR.

In the course of the syntheses of (−)-corynantheidine[1] and dimethoxydespyrrolocorynantheidine,[2] the preparation of the target compounds with *allo* stereo-structure had been realized via unsaturated cyanoacetic acid ester derivatives **1** and **2a**. These compounds are geometrically uniform, and of proved E configuration.[1,2]

Compounds **1** and **2a** can easily be converted by mild oxidation to the amino dienes **3a** or **4a**.[2]

The geometry of the starting compounds which was of uniformly E configuration underwent a change during the formation of the new double bond, so that a mixture of the E and Z isomers was obtained (see Table 1). An isolated carbon–carbon double bond is usually configurationally stable. Nevertheless, in the case of extended conjugation, particularly if there are also electron attracting and electron donor substituents present at the double bond, the rotational potential barrier can decrease to such an extent (ΔG^{+} = 5–25 kcal/mole) that isomerisation can be studied by NMR spectroscopy.[3–7] Using this method, the rotational ΔG^{+} values of the amino dienes **3a** and **4a** have been determined.

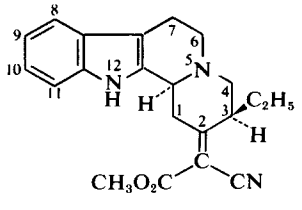
For example, the signals of the ester methoxy protons of compound **3a** in nitrobenzene-d_5 at room temperature appear at δ 3·59 and 3·85 ppm ($\Delta\nu$ = 15·5 Hz), in accordance with the Z and E configurations, respectively. The coalescence temperature (t_c) is 174°, so that ~ 23 kcal/mole was obtained for the free enthalpy of activation (ΔG^{+}) for the rotation about the double bond on the basis of Eyring's relationship.[8] When the solution is cooled again to room temperature, the original spectrum is obtained, which points to the thermodynamic equilibrium between the two isomers.

The fact that the geometrical isomers cannot be separated by the usual preparative techniques is also due to the relatively low ΔG^{+} value of the isomerisation.

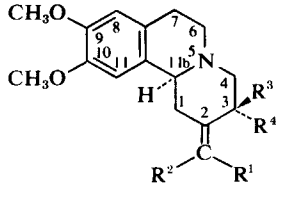
The assignment of the NMR signals of **4a** to the E and Z geometrical isomers was facilitated by the preparation of the corresponding amino diene **4f** from the unsaturated dinitrile **2f**, which as expected proved to be a uniform product.

For the further investigation of the geometrical isomerisation the unsaturated esters **2c** and **2d** were also oxidised. These had been previously prepared,[9,10] and their structures have been proven.[9] As a result of the oxidation reaction, the E and Z isomers of the amino diene **4c** were formed in the same ratio from either compound. The rotational ΔG^{+} value for isomerisation about the carbon–carbon double bond is already so high for this compound that a change cannot be observed below 190° by NMR spectroscopy and ΔG^{+} must be larger than 25 kcal/mole (see Table 1).

*Research Institute for Pharmaceutical Chemistry Budapest, Hungary.

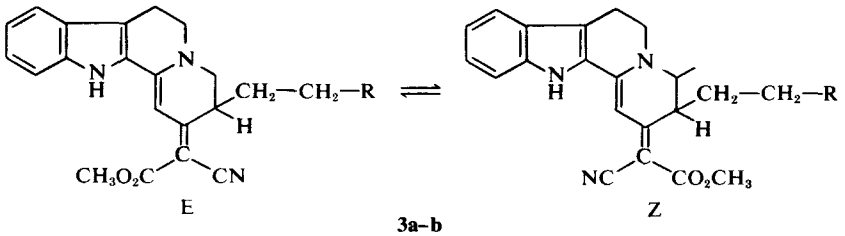


1



2a–f

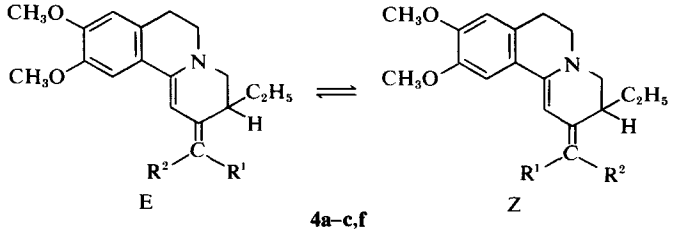
	R^1	R^2	R^3	R^4
2a	CN	CO_2CH_3	C_2H_5	H
2b	CN	$CO_2C_2H_5$	C_2H_5	H
2c	H	CO_2CH_3	C_2H_5	H
2d	CO_2CH_3	H	C_2H_5	H
2e	H	CO_2CH_3	H	C_2H_5
2f	CN	CN	C_2H_5	H



E Z

3a–b

3a R = H
3b R = CO_2CH_3



E Z

4a–c,f

	R^1	R^2
4a	CN	CO_2CH_3
4b	CN	$CO_2C_2H_5$
4c	H	CO_2CH_3
4f	CN	CN

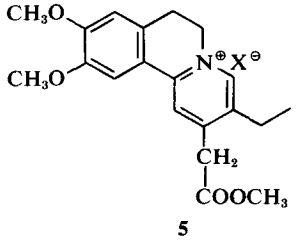
The amino diene **4c** could be prepared also from the unsaturated ester **2e**, epimeric with **2c** and **2d** at C-3.

Upon addition of excess mercuric acetate further oxidation in ring C of the amino diene **4c**, and depending on the pH the tricyclic compounds **5** or **6a** could be obtained. **5** and **6a** could also be prepared directly from the unsaturated esters **2c–e**.

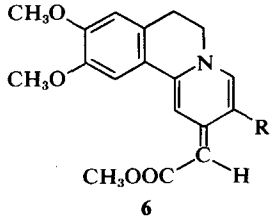
The interconvertibility of **5** and **6a** was proved by a variety of spectroscopic data (Experimental). Because of the introduction of the additional double bond, ring C becomes planar so the Z geometrical isomer of the amino triene **6a** represents a very unfavourable configuration due to steric hindrance. Accordingly, in the NMR spectrum of **6a** only the peaks characteristic of isomer E could be identified. It follows that the $\Delta G^{\ddagger}$ value for the rotation could not be determined by the method adopted in the case of amino dienes. Nevertheless, the effect of the new double bond on the rotational barrier of the exocyclic double bond could be studied on the amino triene **6b**, which contains no substituent at C-3. According to expectations, the further expansion of the conjugation and the possibility of forming an aromatic transitional state result in a decrease of the $\Delta G^{\ddagger}$ value (=CH—$COOCH_3$, $\Delta\nu$ = 10 Hz, t_c = 61°; $\Delta G^{\ddagger}$ = 17·5 kcal/mole).

The $\Delta G^{\ddagger}$ values of the amino dienes of type **3** and **4**, calculated from the data derived from the NMR spectra, as well as the Z/E isomer ratios are summarized in Table 1.

The symmetry of the molecule plays an important role in the mechanism of the rotation about the carbon–carbon double bond. It is presumed that in the case of symmetrically substituted double bonds the radical mechanism predominates, whereas in nonsymmetrical systems the ionic mechanism generally prevails.[3] On this basis, in the case of the asymmetric amino dienes investigated by us, an ionic mechanism is to be expected. The charge separation occurring in the transitional state is stabilized on the one hand by the delocalization effect of the electron attracting nitrile and ester groups, and on the other by that of the electron donating tertiary nitrogen atom and the dimethoxyphenyl group. Accordingly, no radical intermediate product could be detected by ESR studies within the limits of sensitivity of the instrument ($> 10^{-12}$ mole/l). Upon substitution of the nitrile group for hydrogen **4a**→**4c**, higher $\Delta G^{\ddagger}$ values (> 25 kcal/mole) were obtained, a result which sup-



5



6

a R = Et
b R = H

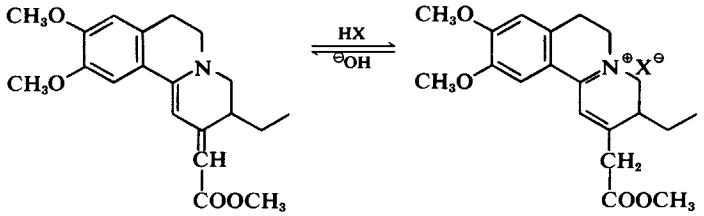
Table 1. $\Delta G^{\ddagger}$ Values of amino dienes of types 3 and 4 calculated from data of the NMR spectra

Compound	Signals observed	$\Delta\nu$ (Hz)	t_c°	$\Delta G^{\ddagger}$ (kcal/mole)	Solvent	Z/E ratio
3a	CO_2CH_3	15·5	174	23·4	$C_6D_5NO_2$	50:50
	CO_2CH_3	15·5	152	22·2	$C_6D_5NO_2$ + CF_3CO_2H ~ 60:1	50:50
3b*	$=C(CO_2CH_3)(CN)$	9·0	169	23·6	$C_6D_5NO_2$	45:55
4a	$-CH_2-CH_3$	3·0	157	23·8		
	11-H	5·5	162	23·6	$C_6C_5NO_2$	33:67
	1-H	80	~ 200	~23·3		
	1-H	82	142	20·2	DMSO-d_6	33:67
4b	$-OCH_2-CH_3$	2·6	157	24·0		
	11-H	5·0	165	23·9	$C_6C_5NO_2$	30:67
4c	$=CH-CO_2CH_3$	22·5	> 190			
	11-H	4·5	> 190	> 25·0	$C_6D_5NO_2$	33:67
	1-H	95	> 190			

*Compound **3b** was prepared as an intermediate for the synthesis of yohimbine derivatives.[11]

ports the ionic character of the transition state for the isomerisation. The $\Delta G^{\ddagger}$ value of the isomerisation of the nitrile ester **3a** decreased on the addition of acid (Table 1).

When the amino diene **4c** was dissolved in HCl, EtOH or AcOH, the migration of the oxocyclic double bond with formation of the conjugated immonium salt **7** (UV, IR, NMR) could be observed.



4c **7**

On the other hand, in the case of the nitrile esters a similar proton addition and double bond migration did not occur as shown by UV spectral evidence.

It can be concluded that rotation about the exocyclic double bond, which occurs in acetic acid during the oxidation of the nitrile esters **1** and **2a–b**, results in formation of the geometrical isomers of the amino dienes **3a** and **4a–b** respectively. On the other hand, the corresponding oxidation of the **2c** and its isomers afford the immonium salt **7** which only on treatment with base affords the geometrical isomers of the amino diene **4c** in a thermodynamically controlled ratio. This observation however does not preclude the possibility of the rotation about the exocyclic carbon–carbon double bond in the case of the amino diene **4c**.

The structural assignments for the amino dienes of type **3** and **4** are supported by mass spectral data. The main fragmentation process is the route of decomposition observed with related compounds: loss of ethylene associated with the McLafferty rearrangement, and subsequent loss of a hydrogen atom, as a consequence of which ring C or D of the skeletal system is aromatised.[2]

EXPERIMENTAL

UV spectra were measured on a Spectromom Model 201 spectrophotometer. IR spectra were recorded in KBr with a Perkin-Elmer Model 457 spectrophotometer. The NMR spectra were obtained using a Varian Model A 60D and JEOL Model C 60HL instruments; chemical shifts are reported as ppm (δ) downfield from TMS. Mass spectra (MS) were recorded with an AEI MS 902 instrument (70 eV, ion source temperature 150°, direct insertion).

The course of the reactions was checked by qualitative thin layer chromatography (TLC), for which Silicagel GF_{254} (Merck) inactive adsorbent was used.

The solutions were evaporated in vacuo, under N_2. Compounds given in the experiments are racemates.

Methyl 3 - ethyl - 9,10 - dimethoxy - 3,4,6,7 - tetrahydro - 2H-benzo[a]quinolizin-$\Delta^{2,\alpha}$-cyanoacetate **4a**

Obtained by the oxidation of the unsaturated nitrile ester **2a**[2] with mercuric acetate. The orange-yellow crystals mp 160–162°,[2] a mixture of the Z and E isomers. NMR ($C_6D_5NO_2$):

	$-CH_2-\underline{CH_3}$	1-H (olefin)	11-H	OCH_3 (9)	8-H
Z	δ 1·13 t	6·38 s	7·23 s	3·82; 3·86;	6·82 s
E	1·16 t	7·77 s	7·32 s	3·95	

UV (EtOH): λ_{max} (log ε): 245 (4·25); 302 (3·82); 344 (3·93); 448 (4·67); 467 (4·70); (0·01N HCl, EtOH): 246 (4·20); 304 (3·82); 344 (3·90); 446 (4·58); 468 (4·62); (glacial AcOH): 302 (3·78); 348 (3·88); 448 (4·57); 466 nm (4·62).

Ethyl 3 - ethyl - 9,10 - dimethoxy - 3,4,6,7 - tetrahydro - 2H-benzo[a]quinolizin-$\Delta^{2,\alpha}$-cyanoacetate **4b**

The unsaturated nitrile ester **2b**[12] (0·384 g; 1 mmole) was dissolved in glacial HOAc (10 ml), a solution of mercuric acetate (0·956 g; 3 mmole) in glacial HOAc (30 ml) was added, and the mixture agitated at 60° for 1 h. After the filtration of the mercurous acetate, the solution was diluted with water (150 ml), the pH of the solution adjusted with 10% aq Na_2CO_3 to pH 6, and the solution extracted with ether. The combined ether phase was washed with 10% Na_2CO_3 and saturated NaCl solutions until it gave a neutral reaction, dried ($MgSO_4$) and evaporated. On triturating the oily residue with hexane, the amino diene **4b** was obtained as an orange-yellow amorphous substance (0·25 g; 65·5%). Anal $C_{22}H_{26}N_2O_4$; 382·4; Calc: N, 7·33; Found: N, 7·60. IR (KBr): 1680 (C=O conj.), 2190 cm^{-1} (C≡N conj.). NMR ($C_6D_5NO_2$):

	$-O\underline{CH_2}-CH_3$	1-H (olefin)	11-H	OCH_3 (6)	8-H
Z	δ 4·33 q	6·37 s	7·23 s	3·87; 3·99	6·85 s
E	4·38 q	7·68 s	7·33 s		

MS: *m/e* (%) 382 (M^+, 100); 381 (6); 354 (29); 353 (79); 337 (21); 328 (14); 309 (14); 307 (7); 281 (9); 280 (7); 270 (5). Mol. wt.: Calc: 382·1885; Found: 382·1892 (MS).

3 - Ethyl - 9,10 - dimethoxy - 3,4,6,7 - tetrahydro - 2H-benzo[a]quinolizin - $\Delta^{2,\alpha}$ - malonic Acid Dinitrile **4f**

The unsaturated dinitrile **2f**[12] (0·337 g; 1 mmole) was dissolved in glacial HOAc (10 ml), a solution of mercuric acetate (0·956 g; 3 mmole) in glacial HOAc (30 ml) was added, and the mixture was agitated at 60° for 1 h. Mercurous acetate precipitated, and was separated by filtration while still hot. Water (~ 100 ml) was added to the filtrate, which was then allowed to crystallize. Orange-yellow crystals separated, which were filtrated, washed with water, and dried over P_2O_5. The amino diene **4f** (0·18 g; 54%) has mp 252–254°. Anal $C_{20}H_{21}N_3O_2$, 335·4. Calc: C, 71·62; H, 6·31; N, 12·53; Found: C, 71·46; H, 6·65; N, 12·42%. IR (KBr): 2180 and 2200 cm^{-1} (C ≡ N conj) NMR ($C_6D_5NO_2$): δ 1·12 (3H, t, $-CH_2-\underline{CH_3}$); 3·79 (3H, s, 9-OCH_3); 3·93 (3H, s, 10-OCH_3); 6·20 (1H, s, olefin-H); 6·82 (1H, s, 8-H); 7·18 ppm (1H, s, 11-H); MS: *m/e* (%) 335 (M^+; 100); 334 (6); 307 (41); 306 (65); 290 (9); 281 (25); 270 (5); 167·5 (M^{2+}; 9); Mol wt: Calc: 335·1634; Found: 335·1636 (MS).

Methyl 3-ethyl-9,10-dimethoxy-3,4,6,7-tetrahydro-2H-benzo[a]quinolizin-$\Delta^{2,\alpha}$-acetate **4c**

(a) The E-unsaturated ester **2c**[9,10] (0·345 g; 1 mmole) was dissolved in glacial HOAc (4 ml), a solution of mercuric acetate (0·956 g; 3 mmole) in glacial HOAc (15 ml) was added, and the mixture is allowed to stand at room temperature for 12 h. The mercurous acetate was filtered off, water (about 150 ml) was added, the pH adjusted with aq ammonia to 6, and the solution extracted with ether. The ether extract was washed with 10% sodium carbonate, then with sat NaCl until neutral. After drying ($MgSO_4$), the solution was concentrated to about 4–5 ml, and allowed to stand. The precipitated yellow **4c** crystals (0·170 g; 50%) had mp 127–129° (ethyl acetate-methanol). Anal $C_{20}H_{25}NO_4$; 343·4, Calc: C, 69·95; H, 7·33; N, 4·08; Found: C, 69·58; H, 7·46; N, 4·22%. IR (KBr): 1680 cm^{-1} (C=O conj.) NMR ($C_6D_5NO_2$):

	$-CH_2-\underline{CH_3}$	$=\underline{CH}-CO_2CH_3$	1-H (olefin)	11-H	8-H
Z	δ 1·13 t	5·53 s	5·90 s	7·28 s	6·70 s
E	1·02 t	5·16 s	7·48 s	7·34 s	

MS: *m/e* (%) 343 (M^+; 48); 342 (9); 315 (34); 314 (100); 312 (23); 284 (7); 282 (7); 270 (9); 256 (7). Mol wt: Calc: 343·1784; Found: 343·1787 (MS) UV (EtOH): λ_{max} (log ε) 237 (4·30); 292 (4·00); 418 (4·45); (0·01 N HCl, EtOH): 234 (3·86); 264 (4·10); 316 (4·14); 396 (3·96); (HOAc): 263 (4·08); 318 (4·14); 396 nm (3·95).

(b) The amino diene **4c**, identical in every respect (IR, NMR, TLC, mp mixed mp) with the product described under (a) was obtained (0·192 g; 56%) from the Z-unsaturated ester **2d**[9,10] according to method (a).

(c) The unsaturated ester **2e**[9,10] (1·04 g; 3 mmole) was allowed to stand in solution with mercuric acetate (4·6 g; 15 mmole) in glacial HOAc (90 ml) at room temp for 48 h. The precipitated mercurous acetate was filtered. According to TLC, the filtrate contained besides the amino diene **4c** also **5** and starting material **2e** (NH_4OH saturation, benzene-methanol 10:1, R_f **2e** 0·48; R_f **4c** 0·6; R_f **5** 0·15). With ice cooling, the filtrate was made just alkaline with aq NH_3, adjusted with a small amount of AcOH to pH 6, and extracted with ether. The ether extract was washed free of HOAc with 10% sodium carbonate, then washed with saturated NaCl solution, dried and evaporated. The oily residue yielded, after treatment with a small amount of ether, crystals of **4c** contaminated with **2e** (0·35 g). Recrystallized from ethyl acetate-methanol, pure **4c** amino diene was obtained (0·25 g; 25%). From the aqueous phase also the overoxidized product was recovered (see following experiment(a)).

Methyl 3 - ethyl - 9,10 - dimethoxy - 6,7 - dihydro - 2H - benzo[a]quinolizin - $\Delta^{2,\alpha}$ - acetate **6a** *and 3 - ethyl - 9,10 - dimethoxy - 2 - methoxycarbonyl - methyl - 6,7 - dihydro - benzo[a]quinolizinium chloride* **5**

(a) The aqueous phase obtained in experiment (c) above was made alkaline with aq ammonia (pH 9), and extracted with methylenechloride. The organic phase was evaporated after drying ($MgSO_4$), and the residue crystallized

from methanol. The greenish-yellow crystals of the amino triene **6a** (0·42 g; 41%) had mp 202·5–204°.

IR (KBr): 1675 (C=O conj) Anal $C_{20}H_{23}NO_4$; 341·39, Calc: N, 4·10, Found: N, 3·93%. NMR ($C_6D_5NO_2$): δ 1·16 (3H, t, CH_2—CH_3); 2·29 (2H, q, CH_2—CH_3); 3·75; 3·82 (6H, s, resp. 3H, s, OCH_3); 4·89 (1H, s, =CH—CO_2CH_3); 6·73 (1H, s, 8-H); 6·86 (1H, s, 1-H); 7·35 (1H, s, 11-H); 8·81 (1H, s, 4-H). UV (EtOH): λ_{max} (log ε): 241 (4·20); 260 (shoulder); 290 (4·08); 317 (4·07); 384 (4·27) (0·01 n HCl, EtOH): 230 (shoulder); 267 (shoulder); 287 (4·18); 369 nm (4·12) see the UV spectrum of **5**. MS: *m/e* (%) 341 (M^+; 100); 340 (33); 310 (50); 298 (12); 283 (50); 282 (46). Mol wt: Calc: 341·1627; Found: 341·1622 (MS).

(b) Amino triene **6a** (50 mg) was dissolved in a 1:1 mixture (5 ml) of methylene chloride-methanol. The solution is slightly acidified with HCl in CH_3OH, evaporated, and the residue was crystallized from methanol-ether. The hydrochloride **5** obtained in an almost quantitative yield, had mp 215° (decomp). IR (KBr): 1740, 1720 (shoulder) (C=O); 1640, 1510 cm^{-1} (pyridinium). NMR ($C_6D_5NO_1$): δ 1·49 (3H, t, CH_2—CH_3); 2·98 (2H, q, CH_2—CH_3); 3·35 (3H, t, 7—CH_2); 3·76 (3H, s, CO_2CH_3); 3·94 (3H, s, 9—OCH_3); 4·13 (3H, s, 10—OCH_3); 4·45 (2H, s, CH_2—CO_2CH_3); 5·18 (2H, q, 6-CH_2); 6·96 (1H, s, 8-H); 7·92 (1H, s, 11-H); 9·15 (1H, s, 1-H); 9·47 (1H, s, 4-H). UV (EtOH): λ_{max} (log ε) 232 (sh.); 268 (sh.); 287 (4·18); 370 (4·15); (0·001N NaOEt, EtOH): 244 (4·25); 267 (shoulder); 293 (4·00); 319 (4·15); 390 nm (4·35), see the UV spectrum of **6a**.

Methyl 9,10-dimethoxy-6,7-dihydro-2H-benzo[a] quinolizine-$\Delta^{2,\alpha}$-acetate **6b**

To a solution of methyl diethylphosphonoacetate (3g; 14·3 mmole) and potassium *t*-butoxide (1·3 g; 11·4 mmole) in DMF (15 ml) 9,10-dimethoxy-1,3,4,6,7,11b-hexahydro - 2H - benzo[a]quinolizin - 2 - one[13] (0·75 g; 2·87 mmole) dissolved in DMF (7 ml) was added. The mixture was allowed to stand overnight at 0° and a further 2 h at room temp. After pouring in ice water the solution was extracted with ether, and the organic phase was thoroughly washed with water, dried and evaporated to dryness. The solution of the oily residue (1·02 g) in HOAc (10 ml) was admixed with mercuric acetate (5·1 g; 16 mmole) dissolved in HOAc (50 ml), and allowed to stand for 48 h at 40°. After filtration of the mercurous acetate precipitate, the solution was poured on to ice-water, neutralized with conc. NH_4OH, treated with a little HOAc (~ 1 ml; pH 6) and extracted with ether. The aqueous layer was made again alkaline with conc NH_4OH (pH 9) and extracted with CH_2Cl_2. The combined CH_2Cl_2 extracts were dried ($MgSO_4$) and evaporated. The residue could be recrystallized from methanol-ether. The greenish-yellow crystals of the amino triene **6b** (0·43 g; 47%) had m.p. 137–142°, and proved to be a mixture of geometrical isomers E and Z (see NMR). Anal $C_{18}H_{19}NO_4$; 313·34 Calc: N, 4·47; Found: N, 4·33%. IR (KBr): 1675 (conj C=O); 1610 (C=C and arom) NMR ($C_6D_5NO_2$): δ 3·77 and 3·85 (6H, OCH_3); 3·77 and 3·93 (3H, CO_2CH_3); 4·95 and 5·05 (1H, —CH—CO_2CH_3); Z/E = 1:1) MS: *m/e* (%) 313 (M^+, 100); 282 (54); 270 (12); 267 (5); 266 (19); 255 (87); 156·5 (M^{++}; 8). Mol wt: Calc: 313·1314: Found: 313·1317 (MS). UV (EtOH): λ_{max} (log ε) 240 (4·15); 259 (sh.); 290 (4·02); 320 (4·03); 378 (4·28). (0·01N HCl, EtOH): 226 (sh.); 266 (sh.); 287 (4·09); 370 (4·11).

Methyl 3-ethyl-3,4,6,7-tetrahydro-2H,12H-indolo [2,3-a] quinolizin-$\Delta^{2,\alpha}$-cyanoacetate **3a**

The amino diene **3a** was prepared from the unsaturated nitrile ester **1**[1] in the way described above (62%). The yellow crystals had mp 237–238° (chloroform-hexane). Anal $C_{21}H_{21}N_3O_2$, 347·4, Calc: C, 72·60; H, 6·09; N, 12·10; Found: C, 72·28; H, 6·31; N, 12·06%. IR (KBr): 3250 (NH); 2200 (C≡N conj.); 1692 cm^{-1} (C=O conj.) NMR ($C_6D_5NO_2$):

	CO_2CH_3	NH	1-H (olefin)
Z	δ 3·85 s	9·90 s	6·37 s
E	3·61 s	10·43 s	

MS: *m/e* (%): 347 (M^+; 100) 346 (15); 332 (5); 319 (40); 318 (83); 316 (18); 293 (18); 288 (15); 286 (15); 260 (6); 259 (10); 258 (6); 249 (7); 173·5 (M^{2+}; 11). Mol. wt: Calc: 347·1634, Found: 347·1630 (MS). UV (EtOH): λ_{max} (log ε): 223 (4·45); 250 (sh); 344 (4·05); 449 (4·70) and 476 nm (4·81). The same UV-curve was also shown in HOAc and in 0·01 N HCl/EtOH.

Acknowledgements—The authors are indebted to Dr József Tamás for the mass spectra and their interpretation. They are also grateful to Dr. László Láng for the UV spectra and to Dr. Béla Mohos for the ESR investigations. For technical assistance, we wish to thank also Mrs S. Krakoviczer and Miss K. Kardulesz.

REFERENCES

[1]Cs. Szántay and M. Bárczai-Beke, *Tetrahedron Letters* 1405 (1968); *Chem. Ber.* **102**, 3963 (1969); *Magy. Kém. Folyóirat* **77**, 170 (1971)
[2]M. Bárczai-Beke, G. Dörnyei, J. Tamás and Cs. Szántay *Chem. Ber.* **105**, 3244 (1972)
[3]H. Kessler, *Angew. Chem.* **82**, 237 (1970) and references cited therein.
[4]Y. Shvo and I. Belsky, *Tetrahedron* **25**, 4649 (1969) and references cited therein.
[5]A. Lidén and J. Sandström, *Tetrahedron* **27**, 2893 (1971) and references cited therein
[6]M. J. S. Dewar and M. C. Kohn, *J. Am. Chem. Soc.* **94**, 2699 (1972)
[7]D. Mörler and F. Kröhnke, *Annalen* **744**, 65 (1971)
[8]H. S. Gutowsky and C. H. Holm, *J. Chem. Phys.* **25**, 1228 (1956)
[9]Cs. Szántay, L. Töke and P. Kolonits, *J. Org. Chem.* **31**, 1447 (1969); *Tetrahedron Letters* 247 (1963); P. Kolonits, *Thesis*, Budapest, 1967.
[10]H. T. Openshaw and N. Whittaker, *J. Chem. Soc.* 1461 (1963)
[11]L. Töke, Zs. Gombos, G. Blaskó, K. Honty, L. Szabó, J. Tamás and Cs. Szántay, *J. Org. Chem.*, in press
[12]A. Brossi and O. Schnieder, *Helv. Chim. Acta* **45**, 1899 (1962)
[13]D. Beke and Cs. Szántay, *Chem. Ber.* **95**, 2132 (1962)