brennung infolge der Oxydationsreaktion auftretende Chemilumineszenz gedeutet werden. Der während der Oxydationsreaktion frei werdende Energiebetrag ist von derselben Grössenordnung wie die entsprechende Energie des blaugrünen Spektralbereiches. So beträgt zum Beispiel die Verbrennungswärme einer C–C-Bindung 49,3 kcal, diejenige einer CS-Bindung 69 kcal[1] usw., das heisst, sie ist von derselben Grössenordnung wie die entsprechende Energie der beobachteten Lumineszenz.

Weiter soll nicht unerwähnt bleiben, dass diese Kontinua erst bei hohem Druck vorkommen und dass ihre Intensität grösser wird, wenn man die Röhre erhitzt. Beide Bedingungen begünstigen ein längeres Verbleiben der primär gebildeten Radikale in der Gasphase und vor allem eine grössere Anzahl aktiver Zusammenstösse; mit andern Worten, sie begünstigen eine grössere Intensität der Emissionskontinua, so wie das beobachtet wird. Die Deutung dieser Kontinua als Rekombinationschemilumineszenz dürfte daher sehr wahrscheinlich richtig sein.

G. MILAZZO

Chemisches Laboratorium, Istituto Superiore di Sanità, Rom, den 10. April 1952.

Summary

The following substances are investigated in emission in the Schüler's discharge tube: furan, pyrrole, thiophen, selenophen, N-methylpyrrole. Different radicals are observed depending on the particular molecule and on the particular pressure range. An emission continuum in the same spectral region and of the same structure for all molecules is also observed.

The resulting electronic configuration of pyrrole is more similar to that of furan than to that of thiophen. On the other hand, the electronic configuration of thiophen together with the electronic configurations of selenophen and N-methylpyrrole are probably similar to that of benzene.

The continuous spectra of emission are interpreted as recombination spectra of the radicals.

[1] F. KLAGES, Ber. dtsch. chem. Ges. *82*, 358 (1949).

Configuration of Dalgliesh's β-p-Nitrophenylserine

Some unsuccessful attempts to obtain β-p-nitrophenylserine by condensation of p-nitrobenzaldehyde and glycine according to D.R.P. 632424[1] led us to prepare this substance by nitration of the diacetate of the phenylserine ethyl ester[2]. The observation by BERGMANN and co-workers (1950)[3] that p-nitrobenzaldehyde and glycine ethyl ester condense easily at room temperature and without a catalyst in alcoholic solution prompted us to resume this work. According to BERGMANN, we obtained the N-p-nitrobenzylidene-β-p-nitrophenylserine ethyl ester (m.p. 140–143°; yield 68%) and the β-p-nitrophenylserine ethyl ester hydrochloride (I) (m.p. 182–184°, decomposition; yield 86%).

Previously DALGLIESH[4] prepared these products using sodium in ether as a catalyst; no attempt was made by him to elucidate their configuration. BERGMANN and co-workers (1951)[5] however pointed out that the configuration of their p-nitrophenylserine is the same as in ERLENMEYER's β-phenylserine, which clearly has been demonstrated[2,6] to be the threo-α-amino-β-hydroxy-β-phenylpropionic acid, since reduction with lithium aluminum hydride led to the threo-2-amino-1-p-nitrophenylpropane-1·3-diol (no experimental details are given). Our experiments on the contrary prove that DALGLIESH's, and therefore BERGMANN's, β-p-nitrophenylserine belongs to the erythro (or allo) series. In fact neutralization of the hydrochloride I yielded the free erythro β-p-nitrophenylserine ethyl ester (II), prismatic needles (from benzene), m.p. 100–103° (found: C, 52·67; H, 5·64; $C_{11}H_{14}O_5N_2$ requires C, 51·96; H, 5·55%). Acetylation of II with acetic anhydride in pyridine gave the erythro N,O-diacetyl-β-p-nitrophenylserine ethyl ester (III), which, after recrystallisation from methanol, had the m.p. 138–139·5° (found: C, 53·45; H, 5·49; $C_{15}H_{18}O_7N_2$ requires C, 53·26; H, 5·36%).

Treatment of II with one mole of dichloroacetyl chloride in tetrahydrofuran yielded equivalent amounts of I and of erythro-N-dichloroacetyl-β-p-nitrophenylserine ethyl ester (IV), cristallising from ethanol in prisms, m.p. 131–132° (sintering at 128°) (found: Cl, 18·56; $C_{13}H_{14}O_6N_2Cl_2$ requires Cl, 19·41%).

[1] Also D. W. WOOLLEY, J. Biol. Chem. *185*, 293 (1950), obtained negative results.

[2] C. G. ALBERTI, B. ASERO, B. CAMERINO, R. SANNICOLO, and A. VERCELLONE, Chimica e Industria *31*, 357 (1949).

[3] E. D. BERGMANN, M. GENAS, and H. BENDAS, C. r. Acad. Sci., Paris *231*, 361 (1950).

[4] C. E. DALGLIESH, J. Chem. Soc. *1949*, 90.

[5] E. D. BERGMANN, M. GENAS, and W. TAUB, J. Chem. Soc. *1951*, 2673.

[6] K. VOGLER, Helv. Chim. Acta *33*, 2111 (1950). – D. BILLET, C. r. Acad. Sci., Paris *230*, 1074 (1950).

		Erythro m. p.	Threo m. p.
p-NO_2·C_6H_4·CHOH·$CHNH_2$(HCl)·$COOC_2H_5$	I	182–184° (decomposition)	153–155° [1] (decomposition)
p-NO_2·C_6H_4·CHOH·$CHNH_2$·$COOC_2H_5$	II	100–103°	115,5–116° [2]
p-NO_2·C_6H_4·CHOAc·CHNHAc·$COOC_2H_5$	III	138–139,5°	122–124° [3]
p-NO_2·C_6H_4·CHOH·$CHNHCOCHCl_2$·$COOC_2H_5$	IV	131–132°	176° [4]
p-NO_2·C_6H_4·CHOAc·$CHNHCOCHCl_2$·$COOC_2H_5$	V	86– 87°	127–128° [4 5]

[1] Prepared from threo-β-p-nitrophenylserine ethyl ester (found: Cl, 11·50; $C_{11}H_{11}O_1N_1Cl$ requires Cl, 12·20%).

[2] B. N. FEITELSON *et al.*, J. Pharm. Pharmacol. *3*, 149 (1951).

[3] C. G. ALBERTI, B. ASERO, B. CAMERINO, R. SANNICOLÒ, and A. VERCELLONE, Chimica e Industria *31*, 357 (1949).

[4] G. CARRARA *et al.*, Gazz. Chim. Ital. *80*, 709 (1950). – We thank Professor G. CARRARA, who kindly supplied us a sample of IV (threo); B. N. FEITELSON and co-workers give for this compound the m. p. 145°.

[5] C. F. HUEBNER and C. R. SCHOLZ, J. Amer. Chem. Soc. *73*, 2089 (1951), give a m. p. 108·109° for the same derivative with ½ molecule of water of crystallisation.

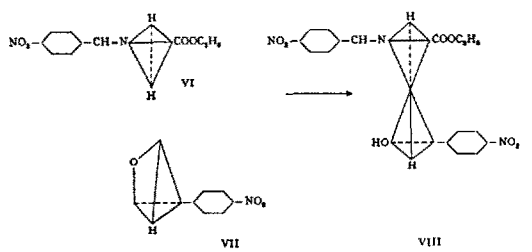
The N-dichloroacetyl derivative IV, acetylated with acetic anhydride in pyridine, gave the crystalline erythro N-dichloroacetyl-O-acetyl-β-p-nitrophenylserine ethyl ester (V) melting at 86–87° (from anhydrous ethanol) (found: Cl, 16·68; $C_{15}H_{16}O_7N_2Cl_2$ requires Cl, 17·41%).

All the above described substances gave a melting point depression when mixed with the corresponding compounds prepared from the threo-β-p-nitrophenylserine ethyl ester obtained by nitration of ERLENMEYER'S β-phenylserine ethyl ester. The para position of the nitro group was determined by alcaline permanganate oxidation to p-nitrobenzoic acid.

The Table page 226 clearly indicates the differences in melting point of the compounds of the erythro and threo series.

As a further proof of the erythro configuration of DALGLIESH'S β-p-nitrophenylserine, we compared the erythro N,O-diacetyl-β-p-nitrophenylserine ethyl ester (III) with an authentic specimen (m.p. 134–136°) synthesized by nitration of the erythro N,O-diacetyl-β-phenylserine ethyl ester prepared following ELPHINOFF-FELKIN and FELKIN procedure[1]: the mixed melting point was undepressed.

In conclusion, the condensation between p-nitrobenzaldehyde (VII) and N-p-nitrobenzylidene-glycine ethyl ester (VI) gives the erythro[2] and not the threo configuration as in the case of benzaldehyde.



VI VII VIII

This fact may perhaps be explained by assuming that during the condensation the two p-nitrophenyl groups repel one another: this causes a trans-orientation of the p-nitrophenyl groups and therefore an erythro configuration in the resulting N-p-nitro-benzylidene-β-p-nitrophenylserine ethyl ester (VIII).

C. G. ALBERTI, B. CAMERINO, and A. VERCELLONE

Research Laboratory, Division of Chemistry, Farmitalia S.A., Milano, January 30, 1952.

Riassunto

Viene dimostrato che la β-p-nitrofenilserina ottenuta per condensazione tra l'etilestere della glicina e la p-nitrobenzaldeide in soluzione eterea in presenza di sodio (DALGLIESH) oppure in soluzione alcoolica da soli (BERGMANN) al contrario della β-fenilserina di ERLENMEYER, possiede la configurazione eritro.

Vengono discussi i motivi di questa diversa configurazione[3].

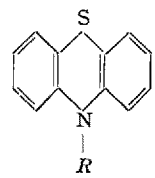
[1] I. ELPHINOFF-FELKIN and H. FELKIN, C. r. Acad. Sci., Paris *232*, 241 (1951).

[2] D. BILLET, C. r. Acad. Sci., Paris *231*, 293 (1950); *230*, 1358 (1950), already doubted DALGLIESH'S β-p-nitrophenylserine was the diastereoisomer of that prepared by nitrating ERLENMEYER'S β-phenylserine.

[3] *ADDED in PROOF.* – Since this note was submitted, we took cognizance from the paper of G. W. MOERSH *et al.*, J. Am. Chem. Soc. *74*, 565 (1952) on the same subject, of the results of M. KOPP *et al.*, C. r. Acad. Science, Paris *233*, 527 (1951), and D. MOLHO and L. MOLHO-LACROIX, ibid. *233*, 1067 (1951), in accordance with ours.

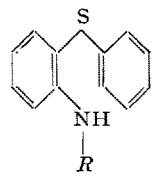
Sintesi di derivati dialchilamminoalchilici dell'o-amminodifenilsolfuro in rapporto ad omologhi della serie della fenotiazina

La sintesi di una serie di derivati N-sostituiti della fenotiazina[1] ha dato un contributo notevole a due campi della farmacologia. Il 3277 R.P. (III, Phenergan, Promethazin) ed il 3015 R.P. (I) si sono inseriti tra i più potenti antiistaminici[2], mentre che il 2987 R.P. (II, Diparcol) ed il 3356 R.P. (IV, Parsidol, Lysivane) hanno trovato un interesse particolare nella terapia del morbo di Parkinson[3].



R: $-CH_2CH_2N(CH_3)_2$ (I)
$-CH_2CH_2N(C_2H_5)_2$ (II)
$-CH_2CH.N(CH_3)_2$ (III)
CH_3
$-CH_2CH.N(C_2H_5)_2$ (IV)
CH_3

Le nostre ricerche su sostanze cardiotossiche[4] della serie dei difenilsolfoni ci hanno indotto ad ideare un tipo di composti derivati dell'o-amminodifenilsolfuro, di struttura talmente vicina a questi derivati della fenotiazina da promettere somiglianze anche nel comportamento farmacologico. Questa speculazione fu appoggiata dal paragone del modello molecolare di un rappresentante della serie fenotiazinica con quello del corrispondente derivato dell'o-amminodifenilsolfuro, che non escludeva una simile disposizione nello spazio, sebbene l'apertura del legame C–N crei nuove possibilità di rotazione.



R	*Kp*	*F*	*F* picrolonato	
$-CH_2CH_2N(CH_3)_2$	1,2 mm 160–162°		171°	(V)
$-CH_2CH_2N(C_2H_5)_2$	0,45 mm 160–161°		138–139°	(VI)
$-CH_2CH.N(CH_3)_2$ CH_3	1,2 mm 177–180°		152°	(VII)
$-CH_2CH.N(C_2H_5)_2$ CH_3	1,2 mm 188–189°	64–66°	152°	(VIII)
$-CH_2CH_2CH_2N(CH_3)_2$	1,3 mm 172–173°		163–164°	(IX)
$-CH_2CH_2CH_2N(C_2H_5)_2$	0,7 mm 185–186°		119°	(X)

Sono stato sintetizzati i prodotti V–X. Di questi è noto soltanto VI, descritto della I. G. Farbenindustrie[5]

[1] H. GILMAN e D. A. SHIRLEY, J. Amer. Chem. Soc. *66*, 888 (1944). – Brit. P. 608208, Société des Usines Rhône-Poulenc in Chemical Abstracts *43*, 2647 (1949). – P. CHARPENTIER, C. r. Acad. Sci. Paris *225*, 306 (1947).

[2] B. N. HALPERN e coll., C. r. Soc. Biol. *140*, 361, 363 (1946); *141*, 1125 (1947). – P. VIAUD, Prod. pharm. *2*, 53 (1947).

[3] J. SIGWALD, D. BOVET e G. DUMONT, Rev. Neurol. *78*, 11 (1946). – C. HEYMANS e coll., Arch. int. pharmacodyn. *79*, 123, 185, 466 (1949).

[4] E. KNÜSLI, Gazz. chim. ital. *79*, 621 (1949); *80*, 522 (1950); Rendiconti Ist. Sup. Sanità Roma *14*, 717 (1951).

[5] DRP. 550327 (1930) in C. 32, II, 1655.