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THE STRUCTURE OF "AZODICHINYL"

F. H. A. RUMMENS and A. C. BELLAART
Laboratories for Instrumental Analysis and Organic Chemistry, Technological University, Eindhoven, The Netherlands

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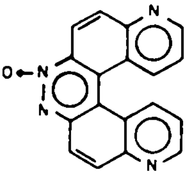
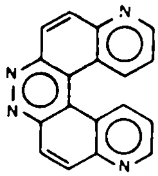
Abstract—The compound $C_{18}H_{10}N_4$ which was subsequently prepared by Knueppel,[1] Meigen[4] and Bellaart[5] is dipyrido[3.2-a: 3'.2'-h]phenazine. This structure was already proposed by Farrar[3] on chemical indications, and has now been proved by spectrometrical means.

BY REDUCTION of 6-nitroquinoline with methanolic sodium methoxide according to Knueppel,[1] an "azoxydichinyl" $C_{18}H_{10}N_4O$ is obtained. When Knueppel distilled the latter compound over iron filings he obtained a compound $C_{18}H_{10}N_4$ which he named "azodichinyl". Knueppel did not indicate the structure of the two compounds. Both compounds were also prepared by Huisgen[2] who ascribed the structure A and B to them without giving any evidence.



A



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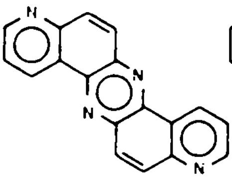

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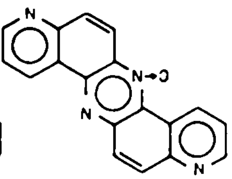


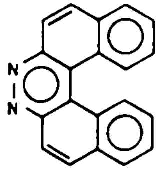
D

Farrar[3] showed that the compound $C_{18}H_{10}N_4$ prepared according to Knueppel[1] and Huisgen[2] is identical with a compound prepared by Meigen[4] from 6-aminoquinoline and from 5-bromo-6-aminoquinoline. Meigen, however, proposed the structure C, based on chemical evidence. One of us,[5] while reducing 6-nitroquinoline with phosphine according to the Buckler method,[6] also obtained a compound $C_{18}H_{10}N_4$ which was subsequently shown to be identical with the corresponding compound of Knueppel and of Meigen.

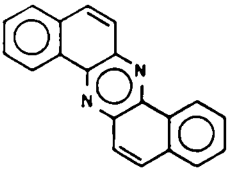
It is clear now that the three mentioned methods of preparation lead to one and the same $C_{18}H_{10}N_4$ compound. This paper intends to elucidate its structure as the arguments of the above mentioned authors do not seem to be sufficiently conclusive. It will be shown by spectrometric means that structure C is the correct one. For this purpose we have also studied two model compounds, i.e. benzo[f]naphtho

[1] C. Knueppel, *Liebigs Ann.* **310**, 75 (1900).
[2] R. Huisgen, *Liebigs Ann.* **559**, 127 (1948).
[3] W. V. Farrar, *J. Chem. Soc.* 799 (1965).
[4] W. Meigen and E. Nottebohm, *Ber. Dtsch. Chem. Ges.* **39**, 744 (1906).
[5] A. C. Bellaart, *Tetrahedron* **21**, 3285 (1965).
[6] S. A. Buckler, L. Doll, F. K. Lind and M. Epstein, *J. Org. Chem.* **27**, 794 (1962).

[2,1-c]cinnoline (structure E) prepared according to Holt and Went[7] and dibenzo [a,h]-phenazine (structure F) which was prepared according to Witt.[8] The correctness of the structures E and F was also confirmed in the process.



E



F

UV spectra

All spectra were recorded in 95% EtOH from 186 to 500 nm on a Cary 14 spectrophotometer. Results are given in Table 1.

TABLE 1

	benzo[f]naphtho-[2,1-c]cinnoline m.p. 270°		dibenzo[a,h]-phenazine m.p. 284°		"azodichinyl" m.p. 369°	
	λ_m(nm)	log ε	λ_m(nm)	log ε	λ_m(nm)	log ε
B-(or α-) band	423·9	3·41	415·2	4·48	392·2	4·16
	401·5	3·38	405·9	4·12	380·5	4·0
			392·5	4·24	371·6	4·08
E_2-(or p-) band	345	4·0	372·0	3·82	353·2	3·87
	329·9	4·21				
E_1-(or β-) band	308·0	4·54	298·3	4·80	299·8	4·92
	272	4·32	292·2	4·83		
	264	4·31				
E_1'-(or β′) band	228·2	4·67	220·4	4·64	212·0	4·59
	204·5	4·74				

These results first of all confirm the assumed structures E and F for benzo[f] naphtho[2,1-c]cinnoline and dibenzo[a,h]phenazine respectively. The higher log ε and lower λ_m for the B and E_1 band as well as the higher λ_m for the E_2 band of the second mentioned compound are indicative. (See also Clar[9]; in particular the spectra of 3·4,5·6-dibenzophenanthrene and 1·2,5·6-dibenzoanthracene given in this reference.)

The high extinction coefficients of the B and E_1 band of the "azodichinyl" compound but in particular the clear separation—both in wavelength and intensity—of the E_1 and E_2 band are taken as evidence for the structure C. The overall similarity with the spectrum of dibenzo[a,h]phenazine, should also be noted.

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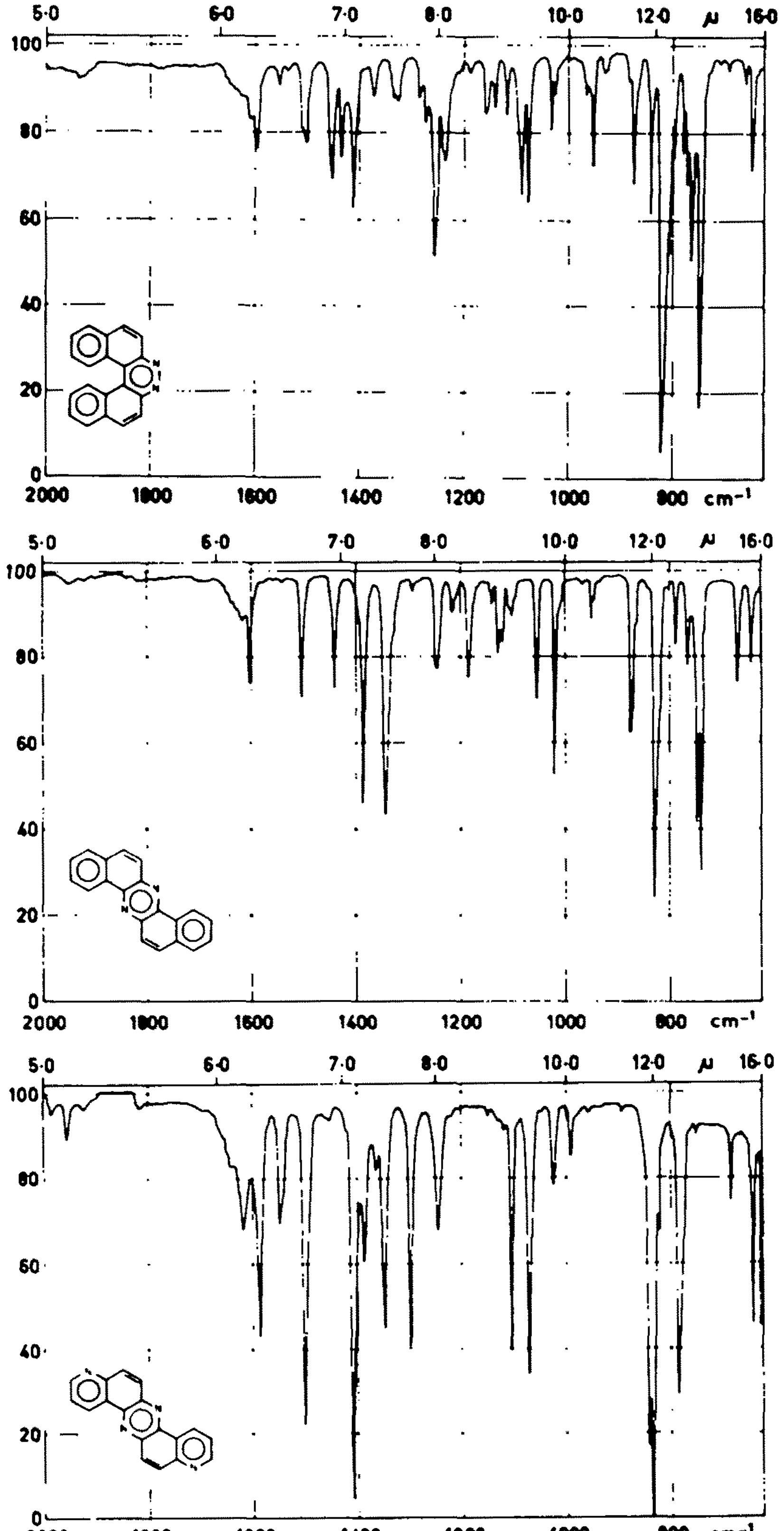
[7] P. F. Holt and C. W. Went, *J. Chem. Soc.* 4099 (1963).

[8] O. N. Witt, *Ber. Dtsch. Chem. Ges.* **19**, 2794 (1886).

[9] E. Clar, *Polycyclic Hydrocarbons* Vol. I. Academic Press (1964).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80
60
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2000
1800
1600
1400
1200
1000
800
cm⁻¹
N
N
N
N

FIG. 1.

IR spectra

Employing the usual KBr pellet sample technique spectra were obtained on Perkin–Elmer model 237 and 137 KBr spectrophotometers over the range 4000 to 400 cm^{-1}.

Benzo[f]naptho[2,1-c] cinnoline showed bands at 1554 cm^{-1} (m) and 955 cm^{-1} (s), which according to Mizushimo *et al.*[10] are characteristic for the pyridazine ring. Similarly dibenzo[a,h]phenazine showed no band in the 1550 cm^{-1} region (the C=N stretching now being symmetry forbidden in IR) and a strong band at 1022 cm^{-1} both facts indicating a pyrazine ring. Along with the naphtyl bands these findings prove the correctness of the structures E and F. The "azodichinyl" has a medium band at 1550 cm^{-1} but this is at least in part due to the quinolyl groups. More significant is the presence of a medium band at 1023 cm^{-1} which is evidence for a pyrazine ring. Spectra of the 2000–625 cm^{-1} region are given in Fig. 1. More information was provided by the 700–400 cm^{-1} region where the skeleton vibrations take place. In Table 2 the results are given. The striking one-to-one correspondence between the frequencies of the second and third column shows that "azodichinyl" must have the same (transoid) skeleton as dibenzo[a,h]phenazine.

TABLE 2. IR FREQUENCIES IN THE 700–400 CM^{-1} REGION

Benzo[f]naptho-[2,1-c]cinnoline (structure D)	Dibenzo[a,h]-phenazine (structure E)	"azodichinyl"
—	676 m	687 m
655 m	649 m	646 m
618 m	—	—
545 m	548 m	545 s
—	540 s	540 m
528 m	—	—
510 w	517 w	512 w
487 w	481 m	486 m
—	437 w	432 m
—	418 w	417 w
409 m	398 m	404 m

The results of this investigation also implicates that "azoxydichinyl" has most likely structure D rather than A as has already been suggested by Farrar.[3]

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[10] M. Ito, R. Shimada, T. Kuraishi and W. Mizushima, *J. Chem. Phys.* 25, 597 (1956).