Photocyclisation of 1,2-Diarylpyridinium Cations and the Photobis-cyclisation of 1,2,6-Triarylpyridinium Cations. *X*-Ray Crystal Structure of 9-Phenyl-2,10b-diazadibenzo[*fg*,*op*]naphthacenium Perchlorate

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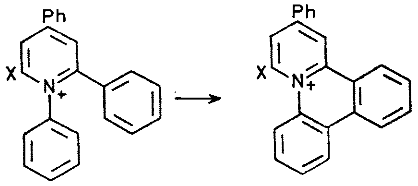
Summary Photobis-cyclisation of 1,2,6-triarylpyridinium cations gives 10b-azadibenzo[*fg,op*]naphthacenium cations (**3a**—**e**) and their 2-aza-analogues (**3f**—**c**); the structures are supported by *X*-ray crystallographic analysis of the 9-phenyl compound (**3f**).

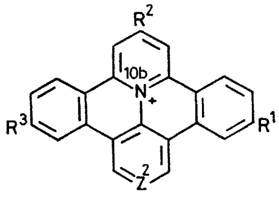
Dorofeenko and his co-workers[1] recently reported the photocyclisation of 1,2-diphenylpyridinium salts (**1a**—**c**) to give fused tetracyclic derivatives (**2a**—**c**). We have confirmed this result for the transformation (**1a**) → (**2a**), but, in our hands, the 1,2,6-triphenyl derivative (**1b**) undergoes bis-cyclisation to the fused hexacycle (**3a**) in 85%

yield.† The considerable scope of the bis-cyclisation is demonstrated by the preparation from the corresponding 1,2,3,4-tetrasubstituted pyridinium salts of three monomethyl derivatives (**3b,c,e**), a trimethyl derivative (**3d**), and the carboxybetaines (**4a—c**). Furthermore, three 1-(4-pyridyl)pyridinium salts gave the corresponding 2,10b-diazadibenzo[*fg,op*]naphthacenium cations (**3f—h**).



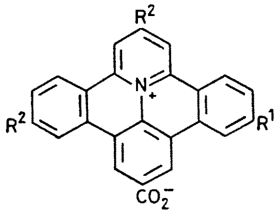
(1) (2)

a, X = Me; b, X = Ph; c, X = CO_2H



(3)

	a	b	c	d	e	f	g	h
R^1	H	H	H	Me	Me	H	H	Me
R^2	Ph	Ph	*p*-Tolyl	*p*-Tolyl	Ph	Ph	*p*-Tolyl	*p*-Tolyl
R^3	H	H	H	Me	H	H	H	Me
Z	CH	CMe	CH	CH	CH	N	N	N



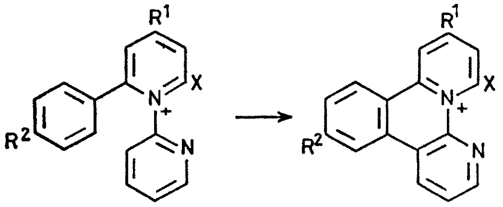
(4)

a, $R^1 = R^2 = H$; b, $R^1 = Me$, $R^2 = H$; c, $R^1 = R^2 = Me$

However, if one of the *ortho*-CH groups in the 1-aryl ring of the original 1,2,6-triarylpyridinium salt was absent, then only monocyclisation occurred. This was illustrated for the series of 1-(2-pyridyl) derivatives (**5a—d**) which cyclised to the benzo[*c*]pyrido[1,2-*a*][1,8]naphthyridinylium cations (**6a—d**). Electron-donor groups appear to inhibit the reaction; no cyclisation was observed with the *o*- or *p*-hydroxy or *o*-methyl derivatives (**7a—c**). Furthermore in the series (**3a**)→(**3b**)→(**3d**) and (**3f**)→(**3g**)→(**3h**) the yield drops with increasing methyl substitution.

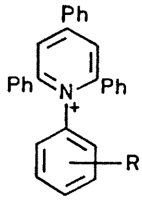
The photobis-cyclisations now reported have analogies in carbocyclic chemistry in the cyclisations of 1,2,3-triphenylbenzene and of 2,2′-diphenylbiphenyl into dibenzo[*fg,op*]naphthacene,[2] but no close heterocyclic analogue is known.[3]

Final confirmation of the structures of our novel bis-cyclisation products was provided by the *X*-ray crystallographic study of the perchlorate salt of (**3f**), dark-brown equidimensional single crystals of which were obtained from Me_2SO–MeOH.



(5) (6)

	a	b	c	d
X	Me	Ph	Ph	*p*-Tolyl
R^1	Ph	Ph	*p*-Tolyl	Ph
R^2	H	H	H	H



(7)

a, R = *o*-OH; b, R = *o*-Me; c, R = *p*-OH

Crystal data: $C_{28}H_{17}ClN_2O_4$, $M_r = 480{\cdot}91$, monoclinic, space group $P2_1/c$, $a = 8{\cdot}962(4)$, $b = 17{\cdot}853(6)$, $c = 13{\cdot}171(5)$ Å, $\beta = 98{\cdot}27(3)^\circ$, $U = 2085$ Å^3, $Z = 4$, $D_c = 1{\cdot}531$ g cm^{-3}, μ (Mo-K_α) = 2 cm^{-1}. The unit cell was measured and intensities ($2^\circ < 2\theta < 50^\circ$) collected using a Syntex $P2_1$ diffractometer with monochromated Mo-K_α radiation, and a crystal 0·4 × 0·3 × 0·2 mm in dimensions. The structure was solved by direct methods using the program SHEL-X. Refinement proceeded to $R = 0{\cdot}058$ for 2373 reflexions with $F > 4\sigma(F)$, with C–H distances fixed at 1·08 Å, and a common isotropic temperature factor for H atoms.‡

The angle between the mean planes of the phenyl ring and the rest of the cation is 159°. The greatest deviation from planarity (excluding the Ph ring) is 0·11 Å; the mean absolute deviation is 0·04 Å.

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† All new compounds reported have given correct analyses.

‡ The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

[1] Ya. R. Tymyanskii, M. I. Knyazhanskii, Yu. P. Andreichikov, G. E. Trukhan, and G. N. Dorofeenko, *Zhur. org. Khim.*, 1976, **12**, 1126 (*Chem. Abs.*, 1976, **85**, 102252f).
[2] T. Sato, S. Shimada, and K. Hata, *Bull. Chem. Soc. Japan*, 1971, **44**, 2484.
[3] F. R. Stermitz, in 'Organic Photochemistry,' ed. O. L. Chapman, Vol. 1, Marcel Dekker, New York, 1967, p. 247.