

## Syntheses and Spectroscopic Studies of 1,8-Bistriazolynaphthalenes

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The first 1,8-diheterocyclic naphthalenes, the 1,8-bis(1'*H*-1',2',3'-triazolyl)naphthalenes (**1a—i**), have been synthesized by 1,3-dipolar cycloadditions of 1,8-diazidonaphthalene to acetylenic esters or enolates of acetoacetic esters, and have strained structures as revealed by comparison of their spectral properties with those of the corresponding 1-(1'*H*-1',2',3'-triazolyl)naphthalenes.

Recently, 1,8-diarylnaphthalenes have been synthesized and studied extensively in view of their geometry and inherent strain due to steric overcrowding.<sup>1</sup> However, heteroaromatic analogues with five-membered heterocyclic rings in the *peri*-position have not yet been studied, presumably because of difficulties in synthesizing them. Thus, we have attempted to synthesize 1,8-bis(1'*H*-1',2',3'-triazolyl)naphthalenes (**1**) by the 1,3-dipolar cycloaddition of 1,8-diazidonaphthalene (**2**)<sup>2</sup> to several dipolaphiles, and have found that a variety of alkoxy-carbonyl derivatives (**1a—h**) and the parent 1,8-bistriazolynaphthalene (**1i**) can be made.

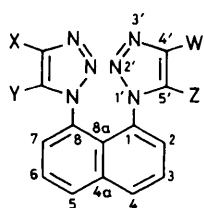
The reactions of (**2**) with a large excess of the acetylenedicarboxylates  $R'O_2CC\equiv CCO_2R'$  ( $R' = \text{Me, Et, Pr}^i, \text{ and Bu}^t$ ),<sup>3</sup> acetylenecarboxylates  $RO_2CC\equiv CH$  ( $R = \text{Me and Et}$ ), or enolates of the acetoacetates  $\text{MeCOCH}_2\text{CO}_2R$  ( $R = \text{Me and Et}$ ) at room temperature in the dark for *ca.* 2 weeks afforded almost quantitatively (**1a**), (**1b—d**) [(**1b**):(**1c**):(**1d**) 30:10:1 for  $R = \text{Me}$ , and 20:10:1 for  $R = \text{Et}$ ], or (**1h**), respectively.

The monotriazolylazides (**3a—d**), formed in the course of the above reactions, underwent further reaction to give the unsymmetrical bistriazolynaphthalenes (**1e—g**).

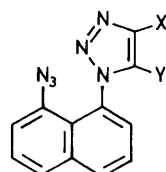
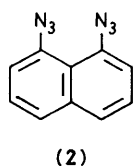
The parent compound (**1i**) was readily synthesized from the carboxylic acids derived from (**1a—f**). Heating crystals of salts of the carboxylic acids up to 180 °C under a nitrogen atmosphere for 1 h afforded (**1i**) almost quantitatively.

The products from the above reactions were isolated by silica gel chromatography and identified by spectroscopic (u.v., i.r., <sup>1</sup>H and <sup>13</sup>C n.m.r.) and elementary analyses.

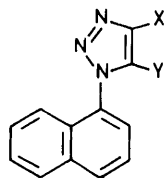
Spectral properties of (**1**) and the corresponding 1-triazolynaphthalenes (**4**), which were prepared by similar methods, are compared and summarized as follows: (i) n.m.r. spectra: in the <sup>1</sup>H n.m.r. spectra of (**1i**), the 4' and 5' protons appeared at higher field by *ca.* 0.5 p.p.m. from those in (**4d**). This suggests that the two triazolyl rings in (**1i**) are facing each other and that their anisotropic effect is comparable to that of the facing benzene rings in 1,8-diphenylnaphthalene ( $\Delta\delta =$



- (1) **a**;  $W = X = Y = Z = \text{CO}_2\text{R}'$   
**b**;  $W = X = \text{CO}_2\text{R}$ ,  $Y = Z = \text{H}$   
**c**;  $W = Y = \text{CO}_2\text{R}$ ,  $X = Z = \text{H}$   
**d**;  $W = X = \text{H}$ ,  $Y = Z = \text{CO}_2\text{R}$   
**e**;  $W = X = Y = \text{CO}_2\text{R}$ ,  $Z = \text{H}$   
**f**;  $X = Y = Z = \text{CO}_2\text{R}$ ,  $W = \text{H}$   
**g**;  $W = \text{CO}_2\text{R}$ ,  $X = Y = \text{CO}_2\text{R}'$ ,  $Z = \text{Me}$   
**h**;  $W = X = \text{CO}_2\text{R}$ ,  $Y = Z = \text{Me}$   
**i**;  $W = X = Y = Z = \text{H}$   
 $\text{R} = \text{Me, Et}$   $\text{R}' = \text{Me, Et, Pr}^i, \text{Bu}^t$



- (3) **a**;  $X = Y = \text{CO}_2\text{R}'$   
**b**;  $X = \text{CO}_2\text{R}$ ,  $Y = \text{H}$   
**c**;  $X = \text{H}$ ,  $Y = \text{CO}_2\text{R}$   
**d**;  $X = \text{CO}_2\text{R}$ ,  $Y = \text{Me}$   
 $\text{R} = \text{Me, Et}$   
 $\text{R}' = \text{Me, Et, Pr}^i, \text{Bu}^t$



- (4) **a**;  $X = Y = \text{CO}_2\text{R}'$   
**b**;  $X = \text{CO}_2\text{R}$ ,  $Y = \text{H}$   
**c**;  $X = \text{H}$ ,  $Y = \text{CO}_2\text{R}$   
**d**;  $X = Y = \text{H}$   
 $\text{R} = \text{Me, Et}$   $\text{R}' = \text{Me, Et, Pr}^i, \text{Bu}^t$

*ca.* 0.5 p.p.m.).<sup>1</sup> <sup>13</sup>C N.m.r. spectra of (1a) showed that the signals of the 4a and 8a carbon atoms shift significantly towards lower field as the alkoxy groups become bulkier. The bulky substituents, then, on the triazole rings seem to increase the strain at the centre of the naphthalene ring.

(ii) U.v. spectra: the u.v. spectra of (1) ( $\lambda_{\text{max}} = 222$  and 288 nm in MeOH), are independent of the substituents on the triazole ring and show a red shift from those of (4) ( $\lambda_{\text{max}} = 221$  and 281 nm in MeOH). Like 1,8-diarylnaphthalenes, which show a similar red shift (*ca.* 10 nm for the longest wavelength bands),<sup>1</sup> there seems to be no significant transannular  $\pi$ -electronic interaction between parallel *peri*-triazole rings.

(iii) I.r. spectra: for (1a–h) and (4a–c), absorptions of C=O (*ca.* 1740  $\text{cm}^{-1}$ ) and C–O–C (*ca.* 1200–1300  $\text{cm}^{-1}$ ) groups were observed in addition to those of the triazole (*ca.* 1000–1100  $\text{cm}^{-1}$ ) and naphthalene rings (*ca.* 750–850  $\text{cm}^{-1}$ ). No significant spectral differences between (1) and (4) were observed, although the spectra of (1) are simpler than those of (4).

Unlike other 1,8-disubstituted naphthalenes<sup>1,4</sup> all the naphthalenes (1) were single substances and no rotamer pairs were obtained even after heating them at 150°C in 1,1,2,2-tetrachloroethane for 5 h. In analogy with 1,8-diarylnaphthalenes, the crowded bistriazolynaphthalenes, such as (1a), might exist as less-strained *trans* conformers because of the very high energy barriers to rotation of the 5'-substituted triazolyl rings, and in the less-crowded naphthalenes like (1b) and (1i), the rotations are probably not restricted, at least at room temperature.

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