On 1,2-Dihydrobenz[*cd*]indazole

By S. BRADBURY, C. W. REES,*† and R. C. STORR†

(*Chemistry Department, The University, Leicester* LE1 7RH)

Summary Attempted preparation of 1,2-dihydrobenz[*cd*]-indazole from dimethyl 1,2-dihydrobenz[*cd*]indazole-1,2-dicarboxylate shows that it exists in more stable tautomeric forms with the aromatic indazole rather than naphthalene nucleus.

WE have previously reported the formation of the 1,2-dihydrobenz[*cd*]indazole derivative (Ia) by addition of 1,8-dehydronaphthalene to dimethyl azodicarboxylate.[1] This compound, and the mono- and di-*N*-oxides of benz-[*cd*]indazole (II) reported by Alder, Niazi, and Whiting[2]

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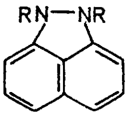
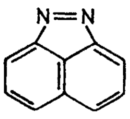
† Present address: Department of Organic Chemistry, University of Liverpool, Liverpool L69 3BX.

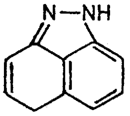
constitute the only authentic examples of naphthalene compounds with a *peri*-N–N bond (see however ref. 3). Previous reports of this system are incorrect or irreproducible (see ref. 1).



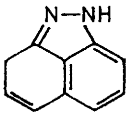
(I) a; $R=CO_2Me$
b; $R=H$



(II)



(III)



(IV)

We assumed that diester (Ia) would be readily converted into 1,2-dihydrobenzindazole (Ib), but treatment with ethanolic potassium hydroxide gave a deep purple solution from which two isomeric colourless indazoles (III) and (IV) were isolated. These can be separated chromatographically on silica gel but they interconvert slowly on standing and rapidly on heating or on treatment with base. Structures (III) and (IV) are based on analytical, spectroscopic, and mass spectral data, on unsaturation towards potassium permanganate, and on the H-bonded association (i.r., osmometric molecular weight) in nonpolar solvents, typical of indazoles. Furthermore an identical mixture was formed, in a standard indazole synthesis, by diazotisation of 5,8-dihydro-1-aminonaphthalene, readily obtained from 1-aminonaphthalene.[4] Reduction of the *N*-oxides of (II) also gave the same mixture of (III) and (IV).‡ It thus appears that 1,2-dihydrobenz[*cd*]indazole (Ib) prefers to exist as the tautomers (III) and (IV), possibly reflecting differences in strain between the 10π aromatic systems with five- or six-membered *peri*-bridges and differences in resonance energy between indazole and naphthalene. An analogous carbocyclic example[5] suggests that strain may be the dominant factor.

The indazoles (III) and (IV) can be re-converted into the *NN′*-dihydro-compound (Ia); thus methyl chloroformate and triethylamine gave (Ia) identical with that from 1,8-dehydronaphthalene and dimethyl azodicarboxylate. This provides a new route to 1,2-disubstituted benz[*cd*]indazoles from 1-aminonaphthalene.

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