NN-Linked Biazoles. Part 2.[1] Attempted Routes to the Benzimidazol-1-yl Radical. Synthesis of 2,2'-Dimethyl-1,1'-bibenzimidazole

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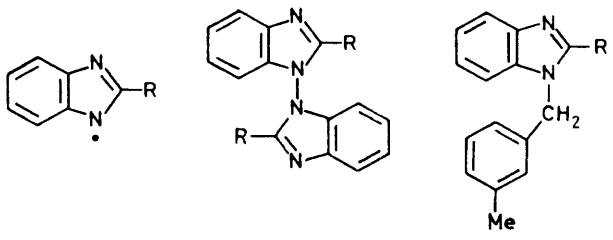
A synthesis of a 1,1'-bibenzimidazole (2; R = Me), through two successive heterocyclizations on 2,2'-azoaniline, is reported. Alternative routes to (2) by direct formation of the N–N bond from the appropriate *N*-substituted-benzimidazoles were unsuccessful, The dimer (2) shows great thermal and photochemical stability towards hydrogen abstraction and addition to olefins. Although the N–N bond can be easily cleaved by irradiation in ethanol, all attempts to detect the neutral radical benzimidazol-1-yl (1; R = Me) from (2) have been unsuccessful. Hydrogen abstraction by (1) is, however, observed with 1-iodobenzimidazole as the precursor.

DESPITE the growing interest in the chemistry of *N*-azolyl radicals, initiated in 1970 by Wang's proposal of imidazol-1-yls as intermediates in the key process of oxidative phosphorylation,[2] most of these radicals remain as yet unknown. An important exception is imidazol-1-yl itself, which was observed by Neta,[3] after addition of OH radicals to imidazole at pH 10—12 and subsequent elimination of water. The same procedure for pyrazole gave no elimination, and an alternative approach to pyrazol-1-yl by irradiation of butylpyrazole-1-percarboxylate in the cavity of an e.s.r. spectrometer was unsuccessful, although some reactions of the radical were described.[4] The rest of the *N*-azolyls hitherto studied belong to a group of highly stabilized systems, like tetra-arylpyrroles,[5] triarylimidazoles (lophines),[6] or carbazoles.[7] Similarly, benzimidazol-1-yl (1), to the best of our knowledge, has never been directly observed,† but its participation in the formation of bibenzimidazoles has been invoked.[9,10] For all *N*-azolyls both a π-type (five π-electrons over five centres) and a σ-type (six π-electrons) ground state can be envisaged.[11]

As an outcome of our interest in the chemistry of



(1) (2) (3)

NN'-linked biazoles, we decided to explore the generation of benzimidazol-1-yl (1) from 1,1'-bibenzimidazole, (2). *NN'*-Linked biazoles could in fact be considered as good precursors for *N*-azoyls, provided that the dissociation energy of the N–N bond is low enough to allow its thermal or photochemical cleavage.‡

Many *CC*-linked dimers of benzimidazole are easily obtainable by trivial procedures. Thus, 2,2'- and 5,5'-bibenzimidazoles result from the reaction of the appropriate diamines with oxalic and formic acid derivatives, respectively.[13] On the other hand, *CN*-linked dimers as 1,2'-bibenzimidazoles are simply obtained when benzimidazoles and 2-chlorobenzimidazoles are heated together.[14] No similar situation holds, however, for the *NN'*-linked dimer (2) which remains hitherto unreported. The only published attempt to synthesize (2) was described in 1963 by Hill, who treated silver benzimidazole with iodine, obtaining 2,2'-bibenzimidazole in 27% yield, instead of the expected dimer (2).[9] In our hands, however, the same experiment, carried out either with 2-substituted or unsubstituted benzimidazoles, yielded only an equimolecular mixture of 1-iodobenzimidazole and starting material. Refluxing this mixture in ethane-1,2-diol, in the hope of substituting iodine by benzimidazole, caused the reduction of 1-iodobenzimidazole to benzimidazole, but we were unable to isolate any dimer from the reaction. If *m*-xylene was used as the solvent, the corresponding 1-(*m*-tolylmethyl)benzimidazoles (3; R = H, Me) were obtained. The same result, though in lower yield, was observed in the absence of the silver salt. Hydrogen abstraction from the solvent proves the participation of radical (1) in the process.

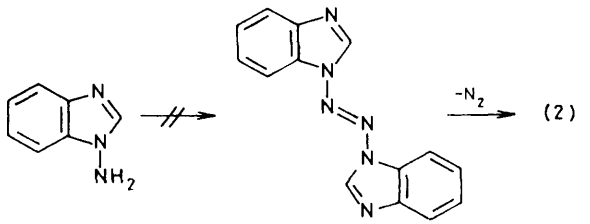
In fact, any approach to *NN'*-linked biazoles based on a direct displacement of an *N*-substituent by an azolyl anion seems hopeless, if we take into account all the examples described so far in other series: Rees and coworkers were unable to react 1-chlorobenzotriazole with sodium benzotriazole,[15] and nucleophilic displacements on 1-nitropyrazoles by pyrazole have been recently reported to yield not 1,1'-bipyrazoles, but 1,3'-bipyrazoles instead, through a *cine*-substitution mechanism.[16] On the other hand, 1-iodobenzimidazole is known to iodinate aromatic amines,[17] and must therefore be considered as a source of positive rather than negative iodine, in agreement with the stability of the benzimidazolyl anion. Hence, it is not surprising that, even under more suitable conditions, as with an homogeneous

† The structure of 2-phenylphenanthro[9,10-*d*]imidazolyl,[8] is closer to a lophine-like radical than to a benzimidazolyl.

‡ Some MNDO calculations, carried out on *NN'*-linked biazoles, show a rather low dissociation energy for the N–N bond (*i.e.* 25.6 kcal mol^{-1} for 1,1'-bipyrazole); however, as MNDO overestimates radical stability, the actual dissociation energy can be somewhat higher.[12]

solution of the reagents in dimethyl sulphoxide (sodium instead of silver benzimidazole), the desired substitution did not take place.

Another approach to the N–N bond could be through the intermediacy of 1,1′-azobisbenzimidazole (5). Sakai and Anselme have reported a synthesis of 2,2′-biindazole by oxidation of 2-indazolylamine with



(4) (5)

mercury(II) oxide, though in poor yield.[18] However, our attempts to prepare (5) by this route from benzimidazol-1-ylamine (4) failed, the starting material being recovered.

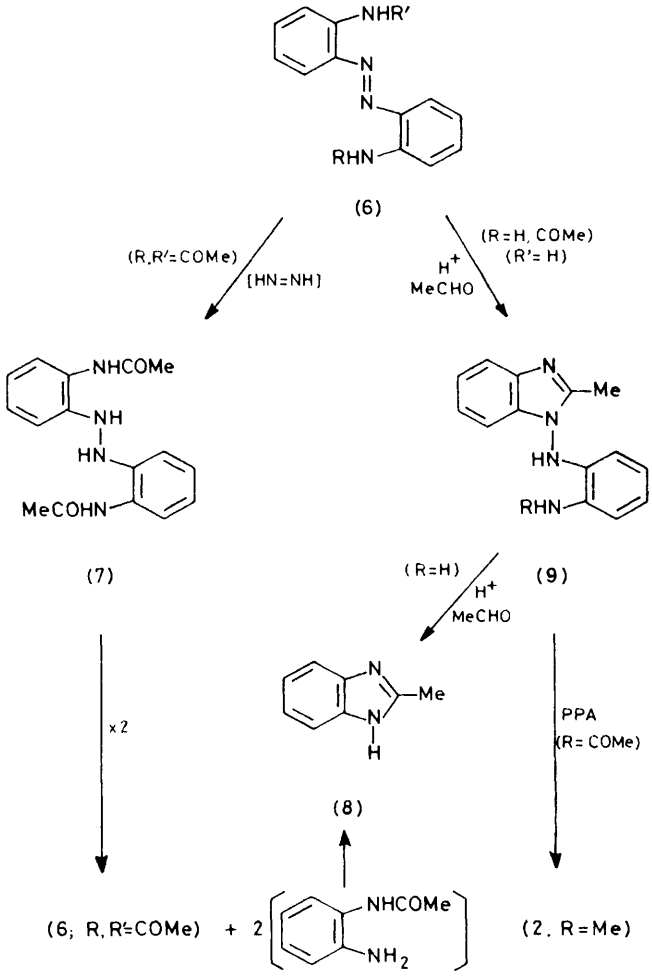
RESULTS AND DISCUSSION

We decided then to start the synthesis of the dimer (2) with a compound carrying the necessary N–N bond, The structure chosen was 2,2′-azoaniline (6; R,R′ = H), readily available by oxidation of phenylene-1,2-diamine. A convenient way to perform the oxidation was found under phase-transfer conditions, and the yield was comparable to that of other more tedious procedures reported,[19]

In order to allow simultaneous cyclization of both rings, 2,2′-azoaniline was reduced with di-imide (from the adduct di-imide–anthracene),[20] but the corresponding hydrazine immediately disproportionated, giving phenylene-1,2-diamine and the starting compound, which was further reduced with the excess of di-imide. Hence, phenylene-1,2-diamine was the only isolated product. Acetyl substitution on (6; R,R′ = COMe) conferred some stability to the reaction product, which could be isolated, but all attempts to cyclize this compound (7) afforded 2-methylbenzimidazole (8) and the precursor (6; R,R′ = COMe), probably through an analogous disproportionation followed by acid-catalysed cyclization of the intermediate monoacetylated phenylene-1,2-diamine.

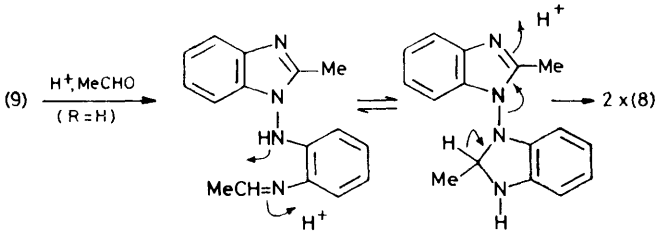
A simple way to avoid the reduction step was found by replacing an aldehyde for one of the two equivalents of the carboxylic acid derivative necessary for the cyclization to the *NN*′-biazole, This was done with the monoacetyl derivative of 2,2′-azoaniline (6; R = COMe, R′ = H), which was transformed in two steps into 2,2′-dimethyl-1,1′-bibenzimidazole. For the last step, polyphosphoric acid was found to be the best reagent. Other methods, like the classical Phillips cyclization of benzimidazoles with aqueous hydrochloric acid,[13] gave the hydrolysed compound (9; R = H), whereas acetic anhydride caused the cleavage of the N–N bond, and azeotropic distillation of water in benzene–toluene-*p*-sulphonic acid gave only poor yields of (2) after long periods of heating.

Finally, acetaldehyde (1 equiv.) cannot be directly used on the unprotected compound (6; R,R′ = H), since the



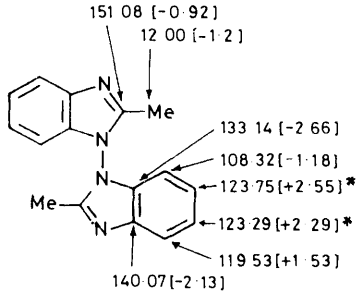
intermediate (9; R = H) rapidly reacts with the unconsumed aldehyde, undergoing N–N bond cleavage to 2-methylbenzimidazole (8), probably through the acid-catalysed process shown.

Structurally, 2,2′-dimethyl-1,1′-bibenzimidazole (2;



R = Me) closely resembles its parent monomer (8), except for the lack of the N–H absorption in the i.r. spectrum, and for its increased solubility in non-polar solvents. The similarities became evident from a

comparison of their u.v. spectra (see Experimental section). The ^{13}C n.m.r. shifts of (2) in [$^2H_6$] dimethyl sulphoxide are shown below. Values in brackets represent the shift differences with 1,2-dimethylbenzimidazole ($\delta_{NN'\text{-dimer}} - \delta_{\text{NMe-deriv.}}$).* The magnitude and sign of the differences completely agree with those found in other *NN'*-linked biazoles. All the structural information suggests a small influence of one ring on the other, and both heterocycles in the dimer probably adopt preferently a twisted conformation, like all the other *NN'*-linked biazoles studied in our laboratory.[1]



(2)

*These assignments can be interchanged

Chemically, the dimer (2) was found to be surprisingly stable to heat and u.v. irradiation. Under most conditions, it was recovered unchanged from sealed tubes heated overnight at 200 °C, either in the presence of olefins or hydrogen donors. Even a radicalophilic olefin, such as α-(t-butylthio)acrylonitrile, which can stabilize radicals by capto-dative substitution,[21] was unable to trap the radical (1; R = Me) from (2). Similar negative results were obtained by photolysis, and attempted detection of the radical (1) in the cavity of an e.s.r. spectrometer were also negative. Neither (1) nor the corresponding 1-oxybenzimidazolyl [irradiation of (2) under oxygen saturation] were observed.† In one case, namely when 2,2'-dimethyl-1,1'-bibenzimidazole was irradiated in ethanol–dichloromethane, a slow decomposition into 2-methylbenzimidazole took place. This result alone cannot be claimed, however, as a proof for the participation of the neutral radical (1) in the process. In fact, protonation of the dimer in the polar solvent could precede its dissociation, giving a radical-cation. In reasonable agreement with this explanation, photolysis of (2) in dichloromethane–HCl-saturated ethanol rapidly gave the cleaved compound in 88% yield. It must be concluded, therefore, that at the present state of our investigation, 1,1'-bibenzimidazoles are not suitable precursors for the generation and/or detection of the neutral radical benzimidazol-1-yl.

EXPERIMENTAL

All new compounds gave satisfactory analysis for C, H, and N, within a 0.3% error. Column chromatography was performed on silica gel (70—230 mesh). All solvents were distilled and carefully dried before use.

Attempted Dimerizations of Benzimidazole.—(a) *Reaction of silver benzimidazole and iodine.* The experimental method described by Hill [9] was repeated. Thus, a solution of iodine (1.27 g, 5.0 mmol) in benzene (25 cm^3) was added dropwise during 1 h to a well stirred suspension of silver benzimidaozle (2.50 g, 0.011 mol) [22] in benzene (75 cm^3), maintained under nitrogen at room temperature. When the iodine colour had completely disappeared (17 h), the resulting suspension was filtered and washed with benzene. The solid was found to be a mixture (i.r.) of the starting silver benzimidazole and 1-iodobenzimidazole as the only organic compounds. The filtrates gave no residue on evaporation. The solid mixture was extracted continuously in a Soxhlet with ethane-1,2-diol, as in Hill's experiment, but 2,2'-bibenzimidazole did not precipitate upon evaporation of the solution and dilution with water. Several days later crystals of benzimidazole developed in the aqueous solution, however, and the residue from the evaporation of the solvent showed intense carbonyl peaks in the i.r. spectrum. Similar results were obtained if 2-methylbenzimidazole was used as starting material.

(b) *Thermal reactions of 1-iodobenzimidazoles.* (i) *With silver benzimidazole in* m-*xylene.* A well stirred mixture of 1-iodo-2-methylbenzimidazole (1.680 g, 6.5 mmol) [17] and silver 2-methylbenzimidazole (1.547 g, 6.5 mmol) in *m*-xylene (100 cm^3) was refluxed for 4 h under nitrogen. The reaction mixture was filtered and washed with ethanol. The filtrates were evaporated and submitted to column chromatography. Chloroform–ethanol (99 : 1) eluted 0.730 g (47%) of 2-*methyl*-1-(m-*tolylmethyl*)*benzimidazole* (3: R = Me), as a colourless oil; δ($CDCl_3$) 2.25 (s, 3 H) and 5.21 (s, 2 H) (xylyl group), 2.52 (s, 3 H, 2-Me), and 6.7—7.3 (m, 8 H, aromatics); $\nu_{max.}$ (NaCl, film) 3 200—2 700, 1 630, 1 565, 1 460, 1 430, 1 395, 1 370, 1 280, 1 230, 1 035, and 740 cm^{-1}; *m/e* 236 (M^+, 15%) and 105 (100%). Further elution with ethyl acetate furnished 2-methylbenzimidazole (1.148 g). An analogous reaction, carried out in the absence of silver salt, gave the same compound (3; R = Me), but in only 8% yield. Essentially the same results were observed starting with 1-iodobenzimidazole, or with ethylbenzene as the solvent.

(ii) *With sodium benzimidazole in dimethyl sulphoxide.* A 2M solution of sodium benzimidazole in dimethyl sulphoxide was prepared as follows: sodium hydride (0.1 mol) and dimethyl sulphoxide (10 cm^3) were allowed to react at room temperature under nitrogen. Benzimidazole (0.1 mol) in dimethyl sulphoxide (40 cm^3) was added dropwise to the resulting suspension, and the whole was stirred until hydrogen evolution ceased. The resulting clear solution was standardized by titration. This solution (1.25 cm^3) and 1-iodobenzimidazole (0.488 g, 2.0 mmol) in dimethyl sulphoxide (50 cm^3) were mixed and stirred under nitrogen at 80—90 °C for 24 h. Solvent was removed at 80 °C/0.3 Torr, and water (100 cm^3) was added to the residue. Unreacted 1-iodobenzimidazole (0.190 g) was filtered off, and the resulting solution, which was alkaline and gave a positive test for iodide ion, was extracted with ether, yielding

* An *N*-substituted model is necessary if annular tautomerism is to be avoided. We are indebted to Dr. A. Fruchier (Université de Montpellier, France) who recorded the spectrum and gave us the data for 1,2-dimethylbenzimidazole.

† The experiments were carried out in dichloromethane at −80 °C [compound (2) alone, and with α-(t-butylthio)acrylonitrile], or at 20 °C [compound (2) under oxygen saturation], trough Pyrex filter, using a 1 000-W high-pressure mercury lamp for the irradiation. We are indebted to Dr. L. Stella (Université d'Aix-Marseille, France) for these e.s.r. experiments.

(column chromatography, eluant chloroform–acetone) benzimidazole (0.317 g) and an unidentified compound (0.025 g) (isomeric iodobenzimidazole?); *m/e* 244 (M^+, 100%) and 117 (67%).

(c) *Attempted oxidation of benzimidazol* 1-*ylamine.* A mixture of benzimidazol-1-ylamine (4) (0.544 g, 4.0 mmol),[1] yellow mercury(II) oxide (Merck) (1.0 g, 4.6 mmol), a catalytic amount of sodium methoxide, and n-butyl alcohol (60 cm³), was stirred under reflux for 50 h. Starting material was recovered in 92% yield from the filtrate. Use of chlorobenzene as the solvent afforded 96% recovery of starting material.

2,2′-*Azoaniline* (6; R,R′ = H).—Phenylene-1,2-diamine (10.8 g, 0.1 mol), methyltrioctylammonium chloride (TOMA) (4.3 g, 0.01 mol), benzene (100 cm³), and 50% aqueous sodium hydroxide (100 cm³) were vigorously stirred for 96 h at 70 °C. The resulting dark mixture was percolated with benzene and the extract submitted to column chromatography (benzene). The yield of compound (6) was 5.0 g (47%), m.p. 133 °C (lit.,[23] 134 °C). Acetylation with an excess of acetic anhydride (reflux, 4 h) gave 2,2′-*azoacetanilide* (6; R,R′ = COMe) in 65% yield, m.p. 273 °C (benzene) (lit.,[23] 271 °C); *m/e* 296 (M^+, 21%) and 134 (100%).

2-*Acetamido*-2′-*aminoazobenzene* (6; R = COMe, R′ = H).—Acetyl chloride (0.392 g, 5.0 mmol) in toluene (50 cm³) was added dropwise (40 min) to a well stirred mixture of 2,2′-azoaniline (1.060 g, 5.0 mmol), anhydrous sodium carbonate (0.50 g), and toluene (100 cm³), maintained at 80—90 °C. Stirring was further continued for 15 min, and the reaction mixture was then evaporated. The residue was treated with water and chloroform, and the organic layer dried and evaporated. Column chromatography (benzene) of the residue afforded 1.022 g (80.5%) of (6; R = COMe, R′ = H) as red crystals, m.p. 143 °C; δ([$^2H_6$]-dimethyl sulphoxide) 2.18 (s, 3 H, MeCO), 3.37 (s, 2 H, NH_2), 6.5—8.2 (m, 8 H, aromatics), and 10.00 (s, 1 H, NH); $\nu_{max.}$ (KBr) 3 490—2 860, 1 680, 1 600, 1 525, 1 485, 1 470, 1 455, 1 425, 1 320, 1 300, 1 235, 1 215, 1 160, 1 130, 760, 740, and 500 cm^{-1}; *m/e* 254 (M^+, 59%) and 92 (100%).

Reduction of 2,2′-*Azoaniline with Di-imide.*—2,2′-Azoaniline (6; R,R′ = H) (0.1 g, 0.47 mmol) and 9,10-dihydroanthracene-9,10-di-imine [20] (0.4 g, 1.88 mmol) were dissolved in ethanol (25 cm³). The solution was refluxed for a few minutes, cooled, and filtered from anthracene. On evaporation, the filtrate yielded phenylene-1,2-diamine (quantitative).

2,2′-*Diacetamidohydrazobenzene* (7).—2,2′-Azoacetanilide (6; R,R′ = COMe) (0.1 g, 0.34 mmol), 9,10-dihydroanthracene-9,10-di-imine (0.423 g, 2.04 mmol) and dimethyl sulphoxide (15 cm³) were stirred for 5 min at 80 °C. The initial orange solution rapidly changed colour to a light yellow. A precipitate formed upon dilution with an excess of water. Further treatment in benzene (300 cm³) under nitrogen afforded 0.038 g of (7) (38%), m.p. 225 °C (decomp.); $\nu_{max.}$ (KBr): 3 370—2 860, 1 655, 1 600, 1 540, 1 520, 1 460, 1 385, 1 300, 1 285, 1 205, 1 180, 1 165, 1 040, 1 015, 760, 750, 685, 625, 575, and 525 cm^{-1}; *m/e* 298 (M^+, 3%) and 108 (100%). From the filtrate, a mixture of anthracene and 2,2′-azoacetanilide was obtained.

Attempts to achieve the acid-catalysed cyclization of (7) (ethanol–HCl, dimethyl sulphoxide–trifluoroacetic acid, or benzene–toluene-*p*-sulphonic acid) gave 2,2′-azoacetanilide and 2-methylbenzimidazole (8).

Reaction of 2,2′-*Azoaniline and Acetaldehyde.*—(a) 2,2′-Azoaniline (0.10 g, 0.47 mmol), acetaldehyde (0.137 g 3.93 mmol), ethanol (10 cm³), and a trace of hydrochloric acid were refluxed together for 1 h. Elimination of volatile materials gave 0.125 g (100%) of 2-methylbenzimidazole.

(b) To a refluxing stirred solution of 2,2′-azoaniline (0.50 g, 2.4 mmol) in ethanol (25 cm³), containing a trace of acid, a solution of acetaldehyde (0.078 g, 0.75 equiv.) in ethanol (25 cm³) was added dropwise during 2 h. Solvent removal gave a mixture (n.m.r. analysis with internal standard) of 2-methylbenzimidazole (1.77 mmol) and unreacted 2,2′-azoaniline (1.47 mmol).

2-(2-*Methylbenzimidazol*-1-*ylamino*)*phenylacetamide* (9; R = COMe).—2-Acetamido-2′-aminoazobenzene (6; R = COMe, R′ = H) (0.60 g, 2.4 mmol), acetaldehyde (0.31 g, 7.0 mmol), a trace of acid, and ethanol (50 cm³) were heated overnight at 90—100 °C in a sealed tube. Column chromatography [chloroform–ethanol (95 : 5)] yielded 0.35 g (53%) of (9) as a colourless solid, m.p. 230 °C; δ([$^2H_6$]-dimethyl sulphoxide) 2.03 (s, 3 H, *N*-acetyl), 2.32 (s, 3 H, 2-Me), 6.7—7.7 (m, 8 H, aromatics), 8.75 (s, 1 H, NH), and 9.56 (s, 1 H, NH); $\nu_{max.}$ (KBr) 3 240—2 820, 1 675, 1 630, 1 610, 1 560, 1 535, 1 510, 1 490, 1 475, 1 460, 1 450. 1 410, 1 375, 1 325, 1 290, 1 240, 765, and 745 cm^{-1}; *m/e* 280 (M^+, 27%) and 132 (100%).

2,2′-*Dimethyl*-1,1′-*bibenzimidazole* (2; R = Me).—2-(2-Methylbenzimidazol-1-ylamino)phenylacetamide (9; R = COMe) (2.14 g, 7.6 mmol), was stirred for 90 min at 140 °C in polyphosphoric acid (38 g). The resulting solution was allowed to cool to room temperature, diluted with water, neutralized to pH 6—7, and extracted with benzene (3 × 50 cm³). The benzene solution, once dried and evaporated, afforded a colourless oil which rapidly crystallized. The solid was further purified by sublimation at 105 °C/0.05 Torr. The yield of purified compound was 2.00 g (92%), colourless crystals, m.p. 139—140 °C; δ($CDCl_3$) 2.37 (s, 6 H, 2-Me), 6.78—7.02 (m, 2 H, 2 × 7-H), 7.10—7.55 (m, 4 H), and 7.75—7.97 (m, 2 H, 4-H and 4′-H); $\nu_{max.}$ (KBr) 3 070, 3 060, 2 930, 2 860, 1 620, 1 550, 1 460, 1 445, 1 385, 1 335, 1 300, 1 290, 1 270, 1 230, 1 020, 865, 770, 750, 745, and 440 cm^{-1}; $\lambda_{max.}$(ethanol) (log ε) 243 (4.26), 274 (3.91), and 280nm (3.95); * *m/e* 262 (M^+, 64%) and 247 (100%).

Reagent mixed with (2; R = Me) (0.19 mmol)	Dichloromethane (cm³)	Product composition [a] (%) (2; R = Me)	(8)
α-(t-Butylthio)-acrylonitrile [24] (0.20 mmol)	10	100 [b]	
m-Xylene (0.20 mmol)	10	76 [b]	16 [b]
Ethanol (5 cm³)	5	56	41
HCl-Saturated ethanol (5 cm³)	5		88

[a] ^{1}H N.m.r. analysis with a known weight of dioxan as internal standard. Differences to 100% are of unidentified tar materials (t.l.c.). [b] The reaction mixture from this experiment did not change its composition under a further 4 h irradiation time, in the presence of a trace of benzoyl peroxide.

Thermal and Photochemical Reactions of 2,2′-*Methyl*-1,1′-*bibenzimidazole* (2; R = Me).—Photolyses were carried out on degassed 0.02M solutions of (2; R = Me) contained in sealed Pyrex tubes. A 500-W Hanau TQ 718 high-pressure mercury burner, immersed in a Pyrex water-cooled jacket, was the light source. The tubes were simply strapped to the external well, and the whole assembly immersed in a water

* 2-Methylbenzimidazole shows absorption at 243 (3.80), 272 (3.91), and 280 (3.89) nm.[25]

bath at room temperature. Irradiation was maintained for 4 h. In each case, a control experiment, without dimer, was carried out in parallel. Results are summarized in the Table.

Similarly, thermolyses were carried out with the same reagents as in the photolyses, in sealed and either degassed or non-degassed 0.1M solutions of (2; R = Me) with *o*-dichlorobenzene as the solvent. The tubes were heated at 200 °C for 15 h, and their contents analysed as before by n.m.r. In all cases, starting materials were quantitatively recovered.

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REFERENCES

[1] Part 1, J. de Mendoza, M. L. Castellanos, J.-P. Fayet, M.-C. Vertut, and J. Elguero, *J. Chem. Research* (*S*), 1980, 50.

[2] J. H. Wang, *Science*, 1970, **167**, 25; J. H. Wang, *Accounts Chem. Res.*, 1970, **3**, 90; S. Tu and J. H. Wang, *Biochemistry*, 1970, **9**, 4505.

[3] A. Samuni and P. Neta, *J. Phys. Chem.*, 1973, **77**, 1629.

[4] J. W. A. M. Janssen, P. Cohen-Fernandes, and R. Louw, *J. Org. Chem.*, 1975, **40**, 915.

[5] W. Brosen, H. Kurreck, D. Rennoch, and J. Reusch, *Tetrahedron*, 1973, **29**, 3959; P.-J. Grossi, L. Marchetti, R. Ramasseul, and A. Rassat, *J. Chim. phys.*, 1967, **74**, 1167.

[6] R. D. Allendoerfer and A. S. Pollock, *Mol. Phys.*, 1971, **22**, 661, and references cited therein.

[7] A. D. McLachlan, *Mol. Phys.*, 1963, **3**, 233; W. A. Waters and J. E. White, *J. Chem. Soc.* (*C*), 1968, 740; T. Shida and A. Kira, *J. Phys. Chem.*, 1969, **73**, 4315; F. A. Neugebauer, H. Fischer, S. Bamberger, and H. O. Smith, *Chem. Ber.*, 1972, **105**, 2694.

[8] Y. Nagai and Y. Sakaino, *Nippon Kagaku Zasshi*, 1969, **90**, 309.

[9] J. H. M. Hill, *J. Org. Chem.*, 1963, **28**, 1931.

[10] S. Ishida, Y. Fukushima, S. Sekiguchi, and K. Matsui, *Bull. Chem. Soc. Japan*, 1975, **48**, 956.

[11] E. M. Evleth, P. M. Horowitz, and T. S. Lee, *J. Amer. Chem. Soc.*, 1973, **95**, 7948; K. Van der Meer and J. J. C. Mulder, *Tetrahedron*, 1976, **32**, 1555.

[12] J. de Mendoza, M. L. Castellanos, N. Roca, S. Olivella, and J. Elguero, unpublished results.

[13] P. N. Preston, *Chem. Rev.*, 1974, **74**, 279.

[14] A. M. Simonov and S. N. Kolodyazhnaya, *Khim. Geterot. Soedineii, Sb.* 1: *Azotsoderhashchie Geterotsikly*, 1967, 141 (*Chem. Abs.*, **70**, 96704b).

[15] C. W. Rees and R. C. Storr, *J. Chem. Soc.* (*C*), 1969, 1474.

[16] P. Cohen-Fernandes, C. Erkelens, C. G. M. Van Eldenburg, J. J. Verhoeven, and C. L. Habraken, *J. Org. Chem.*, 1979, **44**, 4156.

[17] D. Harrison, J. T. Ralph, and A. C. B. Smith, *J. Chem. Soc.*, 1963, 2930.

[18] K. Sakai and J.-P. Anselme *J. Org. Chem.*, 1972, **37**, 2351.

[19] Y. Omote, Y. Nakada, R. Kobayashi, and N. Sugiyama, *Chem. and Ind.*, 1971, **35**, 996.

[20] E. J. Corey and W. L. Mock, *J. Amer. Chem. Soc.*, 1962, **84**, 685.

[21] H. G. Viehe, R. Merényi, L. Stella, and Z. Janousek, *Angew. Chem. Internat. Edn.*, 1979, **18**, 917.

[22] A. J. Cleaver, A. B. Foster, and W. G. Overend, *J. Chem. Soc.*, 1959, 409.

[23] R. Willstätter and A. Pfannenstiel, *Ber.*, 1905, **38**, 2348.

[24] K. D. Gundermann and R. Thomas, *Chem. Ber.*, 1956, **89**, 1263.

[25] D. J. Rabiger and M. M. Joullié, *J. Org. Chem.*, 1964, **29**, 476.