Novel Dimers of 2,2'-(*m*-Phenylene)bis(4,5-diphenyl-1-imidazolyl) Diradical

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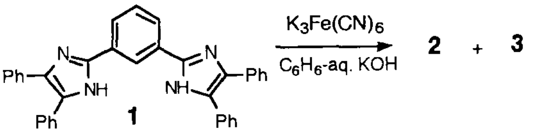
The oxidation of 2,2'-(*m*-phenylene)bis(4,5-diphenylimidazole) **1** with potassium ferricyanide in benzene-aqueous KOH heterogeneous solution gave the diradical dimers **2** and **3**. The dimer **2** showed photochromic and piezochromic properties, whereas the dimer **3** has only photochromic property. The structure of the dimers was deduced by NMR analyses. The X-ray structural analysis revealed that the dimer **3** has a novel *syn*-[3.3]metacyclophane structure.

The chemistry of lophine (2,4,5-triphenylimidazole) has a long history in relation to important physicochemical phenomena such as chemiluminescence[1] through its oxidation and the photo- and piezochromic properties[2,3] of the produced dimer. So far, the proposed dimer structure are based on spectroscopic method, such as IR[3a] and NMR[3b] and no crystal structural data have not been reported. The intervening 2,4,5-triphenyl-imidazolyl radical is stable at low temperature but dimerizes at room temperature. The radical is regenerated by photolysis of the dimers. Thus, these dimers may be used as photo-tunable magnetic materials. We report novel structures of the dimer produced by the oxidation of 2,2'-(*m*-phenylene)bis(4,5-diphenylimidazole) (**1**).

The bisimidazole **1** (2.0 g)[4] was suspended into a benzene (400 ml)-aqueous KOH (400 ml) heterogeneous solution and the oxidation was initiated by the addition of potassium ferricyanide into the mixture. During the addition, the benzene layer gradually turns red-purple and finally fades to yellow (after 1 h at room temperature). From the boundary layer was obtained a pale yellow solid [**2**, 0.456 g, mp 290 °C (decomp.)]. From the benzene layer, another yellow solid (**3**, 1.32 g) was obtained. The yellow **3** was purified by recrystallization from benzene-hexane (yellow prisms, mp 245 °C). The pale yellow **2** obtained from the boundary layer was found to be unstable and gradually converted to **3** in solution. Both compounds **2** and **3** have the same mass of *m/e* = 1025 (M^++H), indicating that they are isomeric dimers. The ^1H-NMR spectrum of **2** measured immediately after dissolution in $CDCl_3$ showed that **2** is almost pure (>90%) and has a considerably different pattern from that of **3**.[5]



The dimer **2** has photochromic property [color turns blue (547 nm in CH_2Cl_2) by irradiation (>310 nm) both in solution and in a solid state] as well as piezochromic property (blue color by grinding). However, the compound **3** showed only photochromic character [551 nm in CH_2Cl_2 after photolysis (>310 nm) at room temperature].

From the analyses of the ^{13}C and C-H COSY NMR spectra, dimer **3** has thirty kinds of carbons with twelve for tetra-substituted carbons including one for tetra-substituted sp^3 carbon (112.7 ppm).[6] The study of the related model compound **4**[6] revealed that this low-field sp^3 carbon is due to that substituted by three nitrogen atoms and one sp^2 carbon. The proton on the C_2-carbon in the *m*-phenylene moiety appears in relatively low field (8.74 ppm) as a singlet. This H_2-proton on the *m*-phenylene showed three kinds of cross-peaks with the other three protons (7.67, 7.46, and 7.08 ppm) on the *m*-phenylene moiety. This indicates that the central benzene ring is asymmetrically substituted. Furthermore, the observation of a single sp^3 carbon at 112.7 ppm indicates that the dimer has two newly formed equivalent carbon-nitrogen bonds. These data accord with the dimer structure of C_2-symmetry. If C_2-symmetry is applied on such a dimer, twenty-eight carbons should be observed by assuming the free rotation of the four phenyl rings. Then, the observed thirty carbons indicate that the dimer **3** in C_2 symmetry has a structure with the restricted bond rotation in one of the phenyl rings. Similar analysis was performed for the dimer **2**, which has a single sp^3 carbon (112.1 ppm) and a single H_2-proton (6.58 ppm) on the *m*-phenylene ring.[5] The large difference in their ^1H NMR spectra is chemical shift values due to the H_2-protons (6.58 for **2**, 8.74 ppm for **3**).

The structure of **3** was successfully determined in explicit manner by the X-ray analysis using imaging plate technique.[7] The dimer **3** has a novel *syn*-[3.3]metacyclophane structure (Figure 1). Syn conformation of the dimer explains the lower chemical shift of H_2-proton on the *m*-phenylene moiety. It is also reasonable to assume that the phenyl ring **A** has a tight environment to restrict its bond rotation (Figure 1).

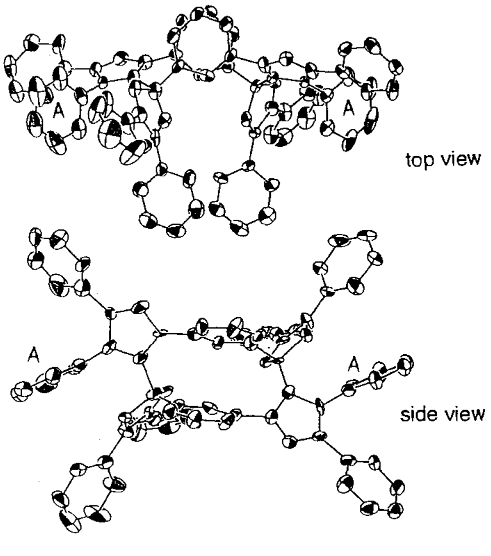
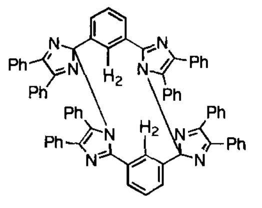
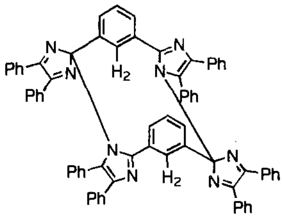


Figure 1. ORTEP view of **3** showing 50% thermal ellipsoids; upper (top view), lower (side view).

Although the structure of the dimer **2** could not be determined clearly because of its instability in solution, the dimer **2** has a similar bond connection sequence from the NMR analyses and is assumed to be a conformational isomer, most likely to be an anti isomer. The isomerization of **2** into **3** accords with this consideration.[8] The proposed structure can be supported by the higher chemical shift value of the H_2-proton which is placed above the benzene ring (*m*-phenylene moiety) and receives a high-field shift by the anisotropic effect of the benzene ring.[9]

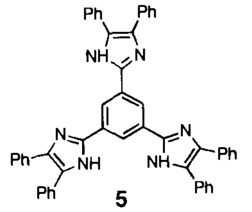


anti somer **2**



syn isomer **3**

As recognized from the relatively congested dimer structure, it may be thought that the dimerization of the related compounds is structure-sensitive. The same type of dimerization was observed in the oxidation of a bis(4,5-dianisyl)imidazole derivative. However, the oxidation of 1,3,5-benzenetriyl (**5**) or 1,8-anthracenediyl linked analogues (**6**) developed a red-purple or orange color, respectively, which persisted for a long time (over 10 h). The resulting solution was ESR active (a broad signal), indicating the participation of stable radicals. However, none of the characterizable radicals or dimers could be isolated from these solutions.



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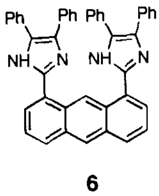

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In short, the oxidation of the bisimidazole **1** gave the radical dimers possessing novel [3.3]metacyclophane structures with photo- and piezochromic properties. The photo-tuning of these dimers as well as structural expansion to their oligomers is in progress.

References and Notes

1 B. Radziszewski, *Ber.*, **10**, 70 (1877); M. Trautz, *Z. Physik. Chem.*, **53**, 86 (1905); T. Hayashi and K. Maeda, *Bull. Chem. Soc. Jpn.*, **35**, 2057 (1962); K. Maeda, H. Ojima, and T. Hayashi, *Bull Chem. Soc. Jpn.*, **38**, 76 (1965).

2 K. Maeda and T. Hayashi, *Bull. Chem. Soc. Jpn.*, **43**, 429 (1962).

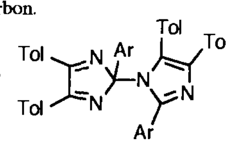
3 a) D. M. White and J. Sonnenberg, *J. Am. Chem. Soc.*, **88**, 3825 (1966). b) H. Tanino, T. Kondo, K. Okada, and T. Goto, *Bull. Chem. Soc. Jpn.*, **45**, 1474 (1972). c) T. Goto, H. Tanino, and T. Kondo, *Chem. Lett.*, **1980**, 431.

4 B. Krieg and G. Maecke, *Macromol. Chem.*, **108**, 210 (1967).

5 Spectral and physical data of **2** and **3**; **2**: pale yellow pawder, mp 290 °C (decomp), ^{1}H NMR (600 MHz, $CDCl_3$) δ 6.58 (s, 2H), 6.87 (d, *J* = 7.1 Hz, 4H), 6.97 (d, *J* = 7.4 Hz, 2H), 7.02-7.14 (m, 6H), 7.19 (t, *J* = 7.7 Hz, 4H), 7.28-7.40 (m, 14H), 7.48-7.59 (m, 10H), 7.74 (d, *J* = 7.7 Hz, 2H), 7.94 (d, *J* = 7.1, 2H), 8.10 (d, *J* = 8.0 Hz, 2H); ^{13}C NMR (151 MHz, $CDCl_3$) (corrected data by subtraction of the signals due to **3** which is produced during the measurement of **2**; the following twenty-four signals are safe to conclude to belong to **2**) δ 112.1, 126.1, 126.8, 127.4, 127.8, 128.4, 128.5, 129.2, 129.6, 130.8, 131.1, 131.2, 131.6, 131.7, 132.3, 132.9, 134.3, 134.4, 135.5, 136.6, 137.0, 148.6, 164.5, 168.0; **3**: yellow prisms, mp 245 °C, ^{1}H NMR ($CDCl_3$) δ 6.94 (d, *J* = 7.7, 4H), 7.04-7.18 (m, 18H), 7.29-7.36 (m, 12H), 7.46 (d, *J* = 7.7 Hz, 2H), 7.53 (dd, *J* = 7.4, 7.7 Hz, 2H), 7.63 (d, *J* = 7.7 Hz, 2H), 7.67 (d, *J* = 8.0 Hz, 2H), 7.70 (d, *J* = 7.1 Hz, 4H), 8.74 (s, 2H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 112.7, 126.2, 127.1, 127.5, 127.7, 127.8, 128.0, 128.3, 128.6(8), 128.7(4), 129.3, 129.8, 130.6, 130.7, 130.8, 131.0, 131.2, 131.3, 131.5, 131.7, 132.0, 132.5, 133.3, 134.3, 134.5, 135.7, 138.0, 147.9, 164.7, 169.2

6 The assignment of the sp^3 carbon was based on the structurally simple model compound, monoradical dimer **4**, which has 112.2 ppm for the sp^3 carbon.

4:

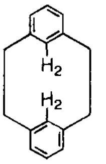


Ar: 3,5-dimethylphenyl
Tol: tolyl

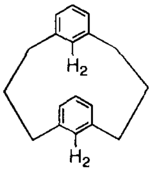
7 X-ray crystallographic analysis was performed on Mac Science-DIP3000 imaging plates. Crystal data for **3**: C72H48N8, monoclinic, space group *P1* (No 1), *a* = 13.672(6), *b* = 14.433(5), *c* = 15.919(8) Å, α = 82.44(3)°, β = 83.21(3)°, γ = 87.68(3), *V* = 3091.16 Å^3, Z = 2, *Dc* = 1.10 gcm^{-3}; Mo-Kα radiation [λ(Kα) = 0.71073 Å]; 15422 unique reflections, of which 7654 were treated as observed [$Fo^2 > 3\sigma(Fo^2)$; *R* = 0.098, *Rw* = 0.175. Because of rather poor refinement factors, the argument on the bond distance and bond angles was avoided.

8 The piezochromic dimer **2** which is metastable amorphous solid would have a weak C-N bond that is cleaved by external mechanical force such as grinding. The development of blue color when grinded would be due to the generation of the imidazolyl radical in a solid state. For this reason, it is not clear whether the isomerization of **2** to **3** in solution proceeds via simple bond rotation without bond cleavage or via C-N bond cleavage mechanism, although the solution isomerization proceeds without color change at room temperature.

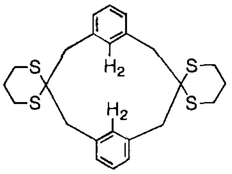
9 In [n.m]metacyclophanes ($2 \le n \le 4$, $2 \le m \le 3$), the H_2-proton in the anti isomer generally appears in higher field than that of the syn isomer as exemplified in the following compounds; see D. Krois and H. Lehner, *Tetrahedron Lett.*, **38**, 3319 (1982), and references cited therein.



anti
4.2 ppm



syn
6.9 ppm



anti
5.8 ppm