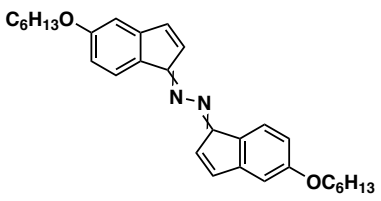
ケタジン骨格を組み込んだビインデニリデンの合成と物性

（京大院工[1]・名大院理[2]・京大 iCeMS[3]）○高木 周[1]・早川 雅大[2]・深澤 愛子[1,3]
Synthesis and Properties of Biindenylidene Bearing Ketazine Skeleton ([1]*Graduate School of Engineering, Kyoto University*, [2]*Graduate School of Science, Nagoya University*, [3]*WPI-iCeMS, Kyoto University*) ○Shu Takagi,[1] Masahiro Hayakawa,[2] Aiko Fukazawa[1,3]

The dense packing of the electron-accepting π-electron systems is expected to acquire excellent electron-transporting properties. Aiming at the development of a novel core skeleton of electron-accepting π-electron systems suitable for this purpose, we now report the design and synthesis of indenone azine derivatives **1**–**3**. We envisioned that these compounds should be highly planar π-electron scaffolds with high electron-accepting property, owing to their structure in which the double bond of pentafulvalene was replaced with a ketazine moiety with the enhanced electron-accepting character without severe steric hindrance. While **1** was obtained as a mixture of three diastereomers owing to the *E/Z* isomerization of C=N bonds, **2** and **3** composed of methoxy and hydroxy group, respectively, at the 7-position of indenone moiety were exclusively obtained as the *E,E*- and *Z,Z*-isomer, respectively, presumably due to the steric effect and the intramolecular hydrogen bonding. Single-crystal X-ray diffraction studies and electrochemical measurements revealed that these compounds have a highly planar structure and a relatively low reduction potential (**2**: $E_{1/2}$ = –1.66 V, **3**: E_{pc} = –1.43 V (vs. Fc/Fc$^+$)). The photophysical properties of **2** and **3** will also be discussed.
Keywords : Ketazine; Biindenylidene; π-conjugation; Electron-accepting character; E/Z isomerization

電子受容性 π 電子系を高密度に集積させることで，突出した電子輸送能の獲得が期待される．本研究では，高密度集積に適した新たな電子受容性 π 電子系の基本骨格の創出を目的に，インデノンアジン誘導体 **1**–**3** を設計，合成した．これらは，ペンタフルバレンに対して電子受容性の高いケタジン部位を挿入した構造をもち，平面性の高さと電子受容性を兼ね備えた基本骨格であると期待される．合成検討の結果，**1** は C=N 結合の *E/Z* 異性化のため 3 種類のジアステレオマー混合物として得られたが，インデノン部位の 7 位にメトキシ基およびヒドロキシ基をもつ **2** および **3** では，置換基の立体効果や分子内水素結合の形成に起因してそれぞれ *E,E* 体，*Z,Z* 体が選択的に得られた．単結晶 X 線構造解析と電気化学測定により，これらの化合物は平面性の高い構造と，比較的低い還元電位 (**2**: $E_{1/2}$ = –1.66 V，**3**: E_{pc} = –1.43 V (vs. Fc/Fc$^+$)) をもつことがわかった．**2** および **3** の光物性についても併せて報告する．



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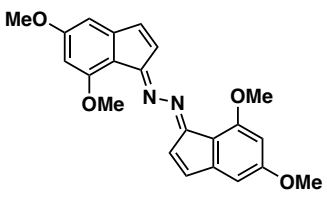

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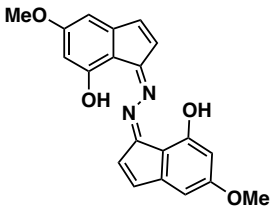

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