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Naphthyl-Substituted Carbocations: From *peri* Interaction to Cyclization

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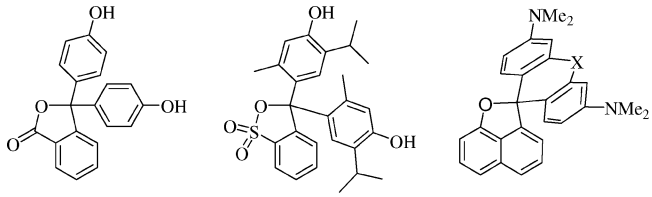
The *peri* interaction of 1-functionalized naphthalenes equipped with a triarylmethyl cation at the 8-position has been studied because of the reversibility of the ring-closing reaction, which was monitored closely by NMR spectroscopy in the case of the cyclic ammonium salt **5b**. Carbocycle **4a** and N-heterocycle **5b** did not exhibit any tendency for ring cleavage under various conditions, whereas the naphtho-annulated furan **4c** underwent reversible ring cleavage under strongly acidic conditions.

Introduction

Triarylmethyl compounds have found widespread application as functional dyes, as exemplified by the prominent indicators phenolphthalein (**1**) and thymol blue (**2**). In structurally related naphthalene derivatives, such as the moderately thermochromic naphthofurans **3**,[1] the ring strain elongates the *peri* bond, classified by Schiemenz and co-workers as the *peri* stress (Scheme 1).[2]



Scheme 1. Examples of classical indicator molecules and thermochromic compounds with a triarylmethyl moiety.

We became interested in naphthyl-substituted triarylmethyl compounds because of their potential as indicators. Compounds with the general structure **4**, equipped with a functional group G with free electron pairs, should be able to coordinate a cationic agent, whereupon the resulting structure **5** could enter an equilibrium with the deeply coloured triarylmethyl salt **6**, depending of course on the strength of the *peri* interaction.[3]

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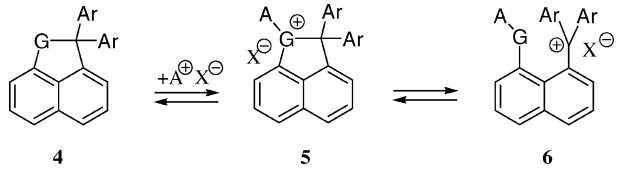
In order to evaluate the equilibria of Scheme 2, we synthesized some naphtho-annulated compounds of the type **4** as well as triarylmethyl salts of type **6** with carbon-, nitrogen- and also oxygen-centred functional units G.

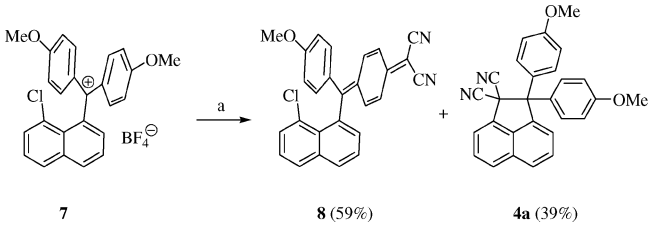


Scheme 2. General concept of a *peri* sensor; Ar = aryl group, A^+ = cationic agent, X^- = corresponding anion, G = functional unit able to coordinate a cationic agent.

Results and Discussion

For the synthesis of the donor–acceptor-substituted acenaphthene **4a**, we chose a one-step transformation of the stabilized triarylmethyl salt **7** that involved a nucleophilic attack of malononitrile followed by an Ullmann-type copper-induced cyclization.[4] Indeed, we obtained a reasonable yield of the target compound **4a**; however, the formation of the *para*-quinoid compound **8** by nucleophilic aromatic substitution was the main reaction pathway, as observed previously with sterically hindered triarylmethyl salts (Scheme 3).[5]

The X-ray crystal analysis[6] of **4a** (Figure 1) clearly reveals a 6% elongation of the central strained C–C bond (164.0 pm compared with the standard bond length of 154 pm of an unstrained C–C bond between sp^3-hybridized centres and even surpasses the elongation of related propellanes).[7] However, despite the impressive bond elongation, **4a** withstands heterolytic bond cleavage under various conditions, as proved by the absence of any change in colour, for instance, when heating the melt to 300 °C in the presence of silver tetrafluoroborate in DMF at reflux tem-



Scheme 3. Synthesis of model compound **4a**. Reagents: (a) malononitrile, NaH, CuBr.

perature or with trifluoroacetic acid in DMSO at reflux temperature, whereas the addition of trifluoromethanesulfonic acid leads to polymeric material. The unreactivity of compound **4a** resembles that of the related push–pull-substituted dihydrophenanthrenes and indanes reported previously by Suzuki and co-workers.[8]

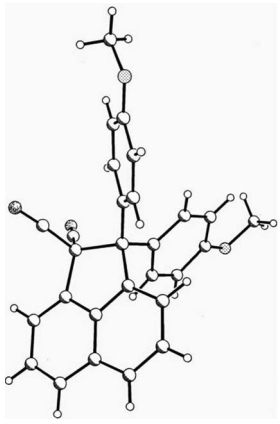
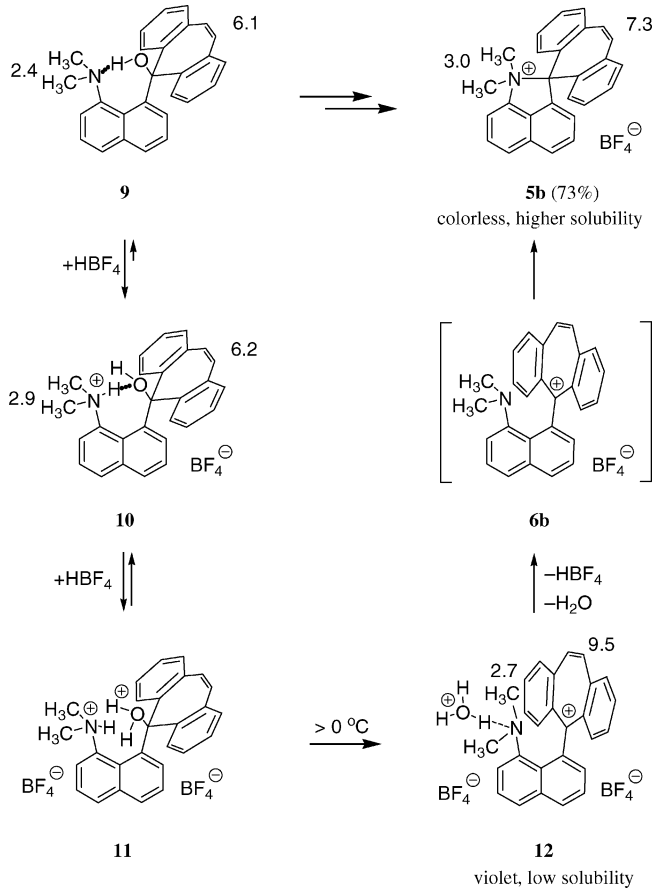


Figure 1. Structure of the strained acenaphthene **4a** in the crystal.[6]

We described the preparation and X-ray crystal analysis of the nitrogen-centred model cationic compound **5b** in an earlier publication.[2] In this work we monitored closely the formation of **5b** by NMR spectroscopy starting from the triarylmethyl alcohol **9** (Scheme 4). The *N*-methyl groups[9] and the olefinic hydrogen atoms of the suberenyl moiety exhibit diagnostic signals throughout the transformation, allowing identification of the reactive intermediates. A sample of **9** in deuteriochloroform at –45 °C was successively treated with 6 equiv. of HBF_4–diethyl ether, whereupon a downfield-shift of 0.4 ppm for the methyl signal was observed, diagnostic of the protonation of the amino group and best described by structure **10** with an intramolecular hydrogen bond and as having a proton-sponge character.[10]

Because of the excess acid, we assumed a dynamic equilibrium with the double salt **11**. The solution was stable in the cold and had a pale-red colour. Above 0 °C, the colour changed to deep-violet, and a second set of signals evolved in the ^{1}H NMR spectrum: a singlet at δ = 9.46 ppm characteristic of the aromatic dibenzosuberenyl cation and a new *N*-methyl signal at δ = 2.71 ppm confirming the cationic character of the amino function, sufficiently explained by structure **12**. Within 4 h at room temperature, this double salt formed a dark precipitate with an almost colourless supernatant, the NMR signals progressively losing intensity. Within another 21 h, the precipitate dissolved again: the slow deprotonation of **12** presumably leads to the short-lived intermediate **6b**. As CIDNP effects are missing from the NMR spectra, we assume that the ring closure to the colourless product **5b** (Figure 2) does not involve radical intermediates. The naphthopyrrolium salt **5b** has been fully



Scheme 4. Intramolecular C–N bond formation at a suberenyl cation, as monitored by ^{1}H NMR spectroscopy ($CDCl_3$); the chemical shifts (δ [ppm]) of the diagnostic signals are given.

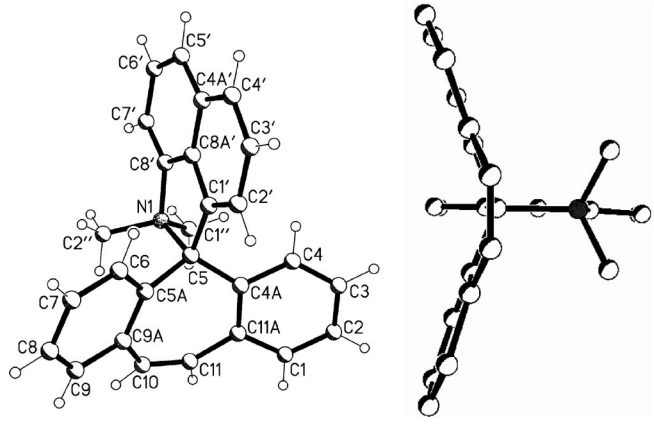
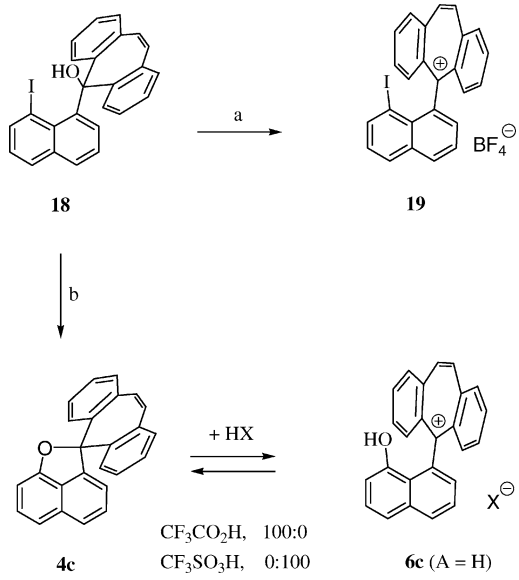


Figure 2. Structure of **5b** in the crystal. Left: Molecular structure of the cation with atom numbering scheme; right: view along the naphthyl moiety.[2]

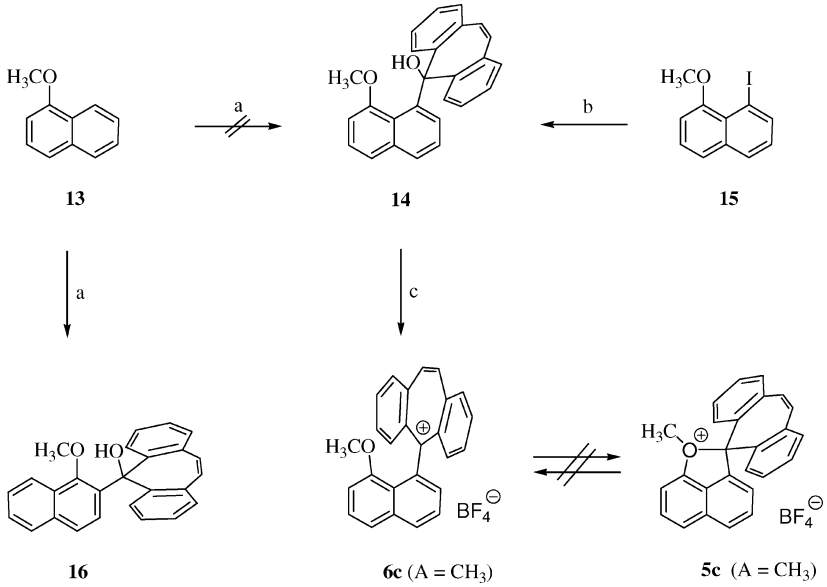
characterized by spectroscopic means and by X-ray crystal analysis.[2] In acetone and in DMSO, the same acid-driven transformation to **5b** takes place, but without detection of **12** as an intermediate, simply because these solvents are more basic than the dimethylamino group in close proximity to the carbocation. Thus, **12** is immediately deprotonated in acetone and DMSO, if formed at all.

The nucleophilicity of an anionic malononitrile group or a dimethylamino group is clearly too high to detect an equilibrium between structures of type **5** and **6**, thus preventing ring cleavage, as proven by our tests with compounds **4a** and **5b**. Therefore, we decided to target the corresponding O-heterocycles, as ether and alcohol moieties are far less nucleophilic.[11] The synthesis of model compound **14** by deprotonation of 1-methoxynaphthalene in the *peri* position failed with *n*BuLi/TMEDA (Scheme 5).[12] Compound **16**, derived from *ortho*-metallation, was exclusively isolated instead, in accordance with recent publications.[13] Therefore, we chose an alternative route to **14**:[14] lithiation of the *peri*-substituted iodonaphthalene **15** and subsequent addition to suberenone was successful and gave a moderate yield of **14**. Transformation to the suberenyl salt **6c** proceeded cleanly. No equilibrium with **5c** was detectable in the ^{1}H NMR spectrum: just one singlet of the olefinic protons at δ = 9.38 ppm, typical of the suberenyl cation. Consequently, we decided to try the reverse transformation: synthesis of the naphthofuran **4c** and subsequent ring cleavage to a structure of type **6** (see Scheme 6).

The sterically crowded suberenol **18** was easily synthesized from 1,8-diiodonaphthalene by initial monolithiation. The corresponding suberenyl tetrafluoroborate **19** was quantitatively obtained by the standard procedure (Scheme 6). Its X-ray crystal analysis revealed that there is no bonding interaction between the suberenyl cation and the iodide in the *peri* position (Figure 3). We synthesized the naphthofuran **4c** by an unusual intramolecular nucleophilic aromatic substitution, profiting from the release of steric strain. Attempts to alkylate **4c** to **5c** with trimethyloxonium tetrafluoroborate or with methyl trifluoromethanesulfonate as an alternative route failed. An equimolar amount of trifluoromethanesulfonic acid (in $CDCl_3$) transformed **4c** quantitatively by ring cleavage to the suberenyl salt **6c**, as revealed by the diagnostic 2-H singlet in the ^{1}H NMR spectrum at δ = 9.10 ppm. In contrast, trifluoroacetic acid is not acidic enough for this transformation. This successful C–O bond cleavage under strongly acidic conditions is of some interest with respect to the recent discussion about the formation of intramolecular triarylmethane/triar-



Scheme 6. Reagents: (a) HBF_4–diethyl ether, dichloromethane, 99%, (b) NaH, THF, reflux, 32%.



Scheme 5. Reagnets: (a) 1. *n*BuLi, TMEDA; 2. suberenone, 82% of **16**; (b) 1. *n*BuLi, 2. suberenone, 43% of **14**; (c) HBF_4–diethyl ether, 97% of **6c**.

ylmethylium complexes with the naphthalene-1,8-diyl skeleton,[15] although the presence of the basic heteroatom in **4c** should make a fundamental difference.

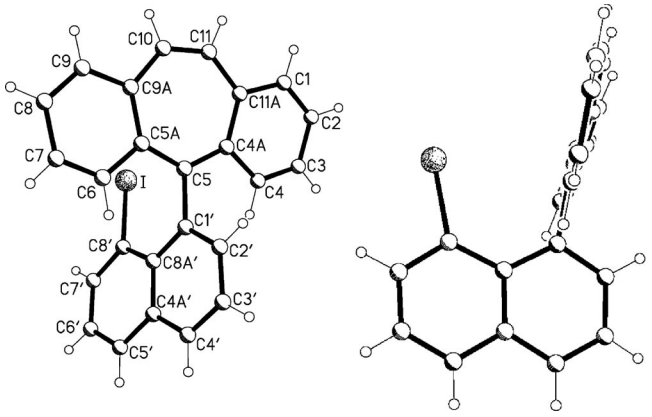


Figure 3. Structure of the cation **19** in the crystal. Left: with atom numbering scheme; right: view along the almost planar 5*H*-dibenzo[*a*,*d*]cycloheptenylium unit.[6]

Conclusions

Among the naphtho-annulated structures **4** and **5** studied, we found acidic reaction conditions for reversible ring cleavage exclusively for the O-heterocycle **4c**, which was monitored by NMR spectroscopy and also noticed directly by the intense colour of the corresponding suberenyl cation of **6c**. Unfortunately, carbocycle **4a** and N-heterocycle **5b** did not exhibit any clear tendency for ring cleavage under a variety of conditions. Future preparative work for the construction of indicators or sensors based on the structural motifs shown in Scheme 2 should focus either on functionalizing the hydroxy group of **6c** or on replacing the methyl groups of **5b** by electron-withdrawing groups such as 2-pyridyl or isoxazolyl groups, thus diminishing the nucleophilicity of the amino group and simultaneously offering coordination sites for transition-metal salts as objects to be sensorily detected.

Experimental Section

General: Melting points (uncorrected) were determined with a Kofler-Heizmikroskop, Modell Reichert Thermovar. Elemental analyses were carried out with a Carlo Erba Elemental Analyser 1106 or a Vario EL instrument. IR spectra (KBr) were recorded with a Bruker Vector 22, a Bruker Equinox 55, a Perkin-Elmer 983G or a Perkin-Elmer 841 spectrometer. UV/Vis spectra were recorded with a Perkin-Elmer Lambda 40 or a Varian Carey 1 spectrophotometer (ε measured in $cm^2\,mmol^{-1}$). ^1H and ^{13}C NMR spectra were recorded with a Bruker DPX 200, WM 300, DRX 400 or DRX 500 spectrometer. Mass spectrometry was performed with a Varian MAT 311 A, AMD 604, MAT CH5 or a VG Autospec spectrometer. For TLC, SiO_2 plates (Polygram SIL G/UV 254) from Macherey & Nagel were used. All compounds were purified by flash chromatography on Kieselgel 60 (Merck, 0.030–0.60 mm). All commercially available products were used without further purification. Compound **7** was synthesized in two steps starting from 1,8-dichloronaphthalene by initial monolithiation with *tert*-butyllithium in THF at –70 °C and subsequent reaction with 4,4′-dimethoxybenzophenone at room temperature (66% yield), followed by treatment with HBF_4–diethyl ether and crystallization from dichloromethane/diethyl ether (97% yield). Preparative procedures for compounds **9** and **5b** have been described earlier.[2]

1,1-Dicyano-2,2-bis(4-methoxyphenyl)acenaphthene (4a) and 2-{4-[(8-Chloro-1-naphthyl)(4-methoxyphenyl)methylene]cyclohexa-2,5-dienylidene}malononitrile (8): A 60% sodium hydride/mineral oil mixture (32 mg, 0.8 mmol) was added to a deep-red solution of tetrafluoroborate **7** (200 mg, 0.421 mmol; see comment above), malononitrile (55 mg, 1.0 mmol) and CuBr (6 mg, 10 mol-%) in dry THF (12 mL), and the mixture was stirred at room temperature for 2 d. A deep-red suspension of tetrafluoroborate **8a** (300 mg, 0.742 mmol) in dry THF (9 mL) was added, and the reaction mixture was stirred at room temperature for 21 h. After hydrolysis with a saturated aqueous $(NH_4)_2HPO_4$ solution (20 mL), the water layer was extracted with diethyl ether (3 × 20 mL), and the combined organic layers were dried with sodium sulfate and the solvents evaporated to dryness with a rotary evaporator. The residue was fractionated by flash chromatography (TLC: silica; diethyl ether/*n*-hexane, 2:3; R_f = 0.27, 0.21). **First Fraction:** 50 mg (29%) of acenaphthene derivative **4a** as colorless crystals; m.p. 222 °C (from CH_2Cl_2/*n*-pentane, 1:3). IR (KBr): $\tilde{\nu}$ = 3037 (w), 2934 (w), 2839 (w), 1608 (m), 1581 (w), 1510 (s), 1461 (w), 1442 (w), 1298 (m), 1257 (s), 1183 (s), 1124 (w), 1031 (m), 820 (m), 811 (m), 801 (w), 790 (w), 776 (m) cm^{-1}. UV (acetonitrile): λ_{max} ($\log\varepsilon$) = 203 (4.80), 219 (4.69, sh), 254 (3.88, sh), 284 (3.85), 308 (3.55, sh) nm. ^1H NMR (500 MHz, $CDCl_3$): δ = 3.78 (s, 6 H, OCH_3), 6.84 (d, J = 9.0 Hz, 4 H, 3′-H, 5′-H, 3′′-H, 5′′-H), 7.30–7.32 (m, 5 H), 7.59 ("dd", "J" = 8.2, 7.1 Hz, 1 H), 7.74 ("dd", "J" = 8.3, 7.1 Hz, 1 H), 7.79 (d, J = 8.0 Hz, 1 H), 7.85 (d, J = 7.0 Hz, 1 H), 7.95 (d, J = 7.9 Hz, 1 H) ppm. ^{13}C NMR (125.8 MHz, $CDCl_3$): δ = 54.81 (s), 55.26 (q, OCH_3), 72.59 (s), 113.97 (d), 114.30 (s), 120.91 (d), 123.99 (d), 124.72 (d), 127.59 (d), 128.85 (d), 129.44 (d), 132.42 (s), 133.13 (s), 134.67 (s), 134.84 (s), 144.47 (s), 159.52 (s) ppm; one missing d is superimposed. MS (EI, 70 eV): *m*/*z* (%) = 417 (31) $[M + 1]^+$, 416 (100) $[M]^+$, 385 (13), 309 (16), 284 (19). $C_{28}H_{20}N_2O_2$ (416.48): calcd. C 80.75, H 4.84, N 6.73; found C 80.97, H 4.77, N 6.82. **Second Fraction:** 66 mg (40%) of *p*-quinodimethane **8** as a green-gold shining solid with m.p. 106 °C. IR (KBr): $\tilde{\nu}$ = 3061 (w), 2932 (w), 2841 (w), 2207 (s), 1607 (m), 1589 (s), 1503 (w), 1452 (m), 1432 (s), 1412 (s), 1260 (s), 1194 (m), 1174 (s), 1025 (w), 840 (m), 821 (m), 765 (m) cm^{-1}. UV (acetonitrile): λ_{max} ($\log\varepsilon$) = 195 (4.63), 213 (4.60, sh), 226 (4.66), 278 (3.85, sh), 308 (4.19), 372 (3.69, sh), 390 (3.84), 522 (4.55) nm. ^1H NMR (300 MHz, $CDCl_3$): δ = 3.85 (s, 3 H, OCH_3), 6.79 (dd, J = 9.6, 2.0 Hz, 1 H, 6-H), 6.90 (d, J = 9.0 Hz, 2 H, 3′′-H, 5′′-H), 6.99 (dd, J = 9.6, 2.0 Hz, 1 H, 5-H), 7.19–7.30 (m, 4 H), 7.42–7.55 (m, 2 H), 7.57–7.62 (m, 2 H), 7.90 (dd, J = 8.0, 1.4 Hz, 1 H), 8.03 (dd, J = 8.3, 1.1 Hz, 1 H) ppm. ^{13}C NMR (125.8 MHz, $CDCl_3$): δ = 55.58 (q, OCH_3), 69.29 (s), 114.10 (d), 115.12 (s), 115.22 (s), 123.47 (d), 123.98 (d), 125.37 (d), 126.86 (d), 128.40 (d), 129.87 (d), 130.64 (s), 131.41 (d), 132.13 (s), 132.14 (s), 132.86 (d), 134.92 (d), 135.98 (s), 136.44 (s), 137.21 (d), 137.64 (d), 155.77 (s), 162.32 (s), 164.09 (s) ppm; one missing s is superimposed, presumably at δ = 129.87 ppm. MS (EI, 70 eV): *m*/*z* (%) = 422 (36) $[M + 1]^+$, 421 (30) $[M]^+$, 420 (100), 386 (8), 385 (26), 384 (9), 341 (10), 314 (11), 312 (13), 279 (11), 276 (12), 143 (13), 138 (11). $C_{27}H_{17}ClN_2O$ (420.90): calcd. C 77.05, H 4.07, N 6.66; found C 76.93, H 4.30, N 6.54.

1-Iodo-8-methoxynaphthalene (15):[14] 1,8-Diiodonaphthalene (500 mg, 1.32 mmol)[16] and CuBr (38 mg, 20 mol-%) were added to a methanolic solution of sodium methoxide, prepared from sodium (50 mg, 2.18 mmol) and dry methanol (13 mL), and the mixture was stirred at reflux temperature for 4 h. After hydrolysis with water (20 mL) and extraction with diethyl ether (3 × 20 mL), the combined organic layers were filtered through a pad of silica and concentrated to dryness; TLC (silica; *n*-pentane): R_f = 0.30, 0.12. The crude product was fractionated by flash chromatography. **First Fraction:** 60 mg (12%) of recovered 1,8-diiodonaphthalene. **Second Fraction:** 216 mg (58%) of **15** as a pale-yellow solid with m.p. 61–62 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.93 (s, 3 H, OCH_3), 6.89 ("dd", "*J*" = 8.9, 6.1 Hz, 1 H), 7.01 ("dd", "*J*" = 8.1, 7.4 Hz, 1 H), 7.34–7.41 (m, 2 H), 7.73 (dd, *J* = 8.2, 1.2 Hz, 1 H), 8.17 (dd, *J* = 7.4, 1.2 Hz, 1 H) ppm. ^{13}C NMR (125.8 MHz, $CDCl_3$): δ = 54.85 (q, OCH_3), 85.42 (s), 106.54 (d), 121.53 (d), 125.23 (s), 126.26 (d), 127.00 (d), 128.76 (d), 136.13 (s), 140.96 (d), 154.30 (s) ppm.

5-Hydroxy-5-(8-methoxy-1-naphthyl)-5*H*-dibenzo[*a*,*d*]cycloheptene (14): A 15% solution of *n*-butyllithium in *n*-hexane (0.5 mL, 0.8 mmol) was added to a solution of 1-iodo-8-methoxynaphthalene (**15**) (200 mg, 0.704 mmol) in dry diethyl ether (10 mL) at –70 °C within 10 min. After 30 min of stirring, 5*H*-dibenzo[*a*,*d*]cyclohepten-5-one (150 mg, 0.704 mmol) in dry diethyl ether (8 mL) was added at –50 °C. The yellow solution was stirred at room temperature for 1 d. After hydrolysis with a saturated aqueous $(NH_4)_2HPO_4$ solution (20 mL), the water layer was extracted with diethyl ether (3 × 20 mL), and the combined organic layers were dried with sodium sulfate and the solvents evaporated to dryness with a rotary evaporator. The crude product (242 mg) was fractionated by flash chromatography (TLC: silica; toluene; R_f = 0.82, 0.49, 0.35). **First Fraction:** 34 mg (28%) of 1-methoxynaphthalene (**13**). **Second Fraction:** 110 mg (43%) of the tertiary alcohol **14** as colourless crystals with m.p. 232 °C (crystallized from toluene). IR (KBr): $\tilde{\nu}$ = 3505 (s), 3053 (w), 3019 (w), 2935 (w), 1616 (w), 1571 (m), 1481 (m), 1459 (s), 1435 (m), 1375 (m), 1331 (m), 1259 (s), 1222 (m), 1174 (m), 1157 (m), 1127 (s), 1070 (s), 1036 (w), 1011 (s), 817 (s), 778 (m), 764 (s), 748 (s), 635 (w), 628 (m), 614 (m) cm^{-1}. UV (acetonitrile): λ_{max} (logε) = 194 (4.56), 222 (4.76), 243 (4.47, sh), 287 (4.07), 331 (3.50, sh) nm. ^{1}H NMR (300 MHz, $CDCl_3$): broad signals were observed due to dynamic effects; δ = 3.45 (s, 3 H), 5.20 (s, 1 H, OH), 6.15 (br. s, 1 H), 6.42 (br. s, 1 H), 6.43 (d, *J* = 7.7 Hz, 1 H), 6.82–7.57 (br. m, 11 H), 8.23 (m, 2 H) ppm. ^{13}C NMR (125.8 MHz, $CDCl_3$): only sharp signals are listed; δ = 54.44 (q, OCH_3), 79.24 (s), 104.22 (d), 121.55 (d), 123.85 (s), 124.36 (d), 125.04 (d), 127.85 (d), 128.32 (d), 135.78 (s), 139.21 (s), 153.87 (s) ppm. MS (EI, 70 eV): *m*/*z* (%) = 364 (28) [M]$^+$, 348 (12), 347 (23), 335 (9), 333 (10), 332 (15), 331 (30), 207 (17), 186 (49), 185 (100), 179 (22), 178 (72), 171 (22), 170 (14), 155 (20), 151 (11), 150 (11), 127 (14), 115 (19). $C_{26}H_{20}O_2$ (364.44): calcd. C 85.69, H 5.53; found C 85.72, H 5.48. **Third Fraction:** 52 mg (35%) of 5*H*-dibenzo[*a*,*d*]cyclohepten-5-one as recovered starting material.

5-(8-Methoxy-1-naphthyl)-5*H*-dibenzo[*a*,*d*]cyclohepten-5-ylium Tetrafluoroborate (6c): HBF_4–diethyl ether (0.09 mL, 0.66 mmol) was added to the tertiary alcohol **15** (60 mg, 0.17 mmol) in dry CH_2Cl_2 (2 mL) at room temperature. After 5 min, stirring was stopped, and a layer of diethyl ether (13 mL) was carefully placed on top of the reaction mixture. After 1 d at room temperature, the precipitate was isolated by filtration, washed with diethyl ether (2 × 2 mL) and dried at 50 °C/0.04 mbar. Tetrafluoroborate **6c** (69 mg, 97%) was obtained as violet needles with m.p. 204–206 °C. The deep-violet solution in $CDCl_3$ did not show any change in colour intensity when cooled to –170 °C. IR (KBr): $\tilde{\nu}$ = 3053 (w), 3020 (w), 2938 (w), 1603 (w), 1571 (w, sh), 1517 (w, sh), 1463 (w, sh), 1428 (m), 1384 (m), 1337 (w), 1256 (w, sh), 1124 (s), 1084 (s, br), 819 (w), 770 (w), 733 (w) cm^{-1}. UV (acetonitrile): λ_{max} (logε) = 211 (4.64), 237 (4.66), 307 (5.08), 376 (3.80), 406 (3.79), 512 (3.62), 542 (3.67) nm. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.81 (s, 3 H, OCH_3), 6.73 (d, *J* = 7.7 Hz, 1 H, 7-H), 7.26 (d, *J* = 6.8 Hz, 1 H, 2-H), 7.59 ("t", "*J*" = 8.0 Hz, 1 H, 6-H), 7.75 ("t", "*J*" = 7.9, 7.2 Hz, 1 H, 3-H), 7.76 (d, *J* = 8.2 Hz, 1 H, 5-H), 7.91–7.97 (m, 2 H, 3′-H, 7′-H), 8.14 (d, *J* = 8.8 Hz, 2 H, 4′-H, 6′-H), 8.22 (d, *J* = 8.1 Hz, 1 H, 4-H), 8.50 ("t", "*J*" = 7.1 Hz, 2 H, 2′-H, 8′-H), 8.87 (d, *J* = 7.7 Hz, 2 H, 1′-H, 9′-H), 9.38 (s, 2 H, 10′-H, 11′-H) ppm. ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 55.68 (q), 107.70 (d, C-7), 121.80 (d, C-3), 124.09 (s), 125.37 (d, C-5), 128.08 (d, C-2), 128.47 (d, C-6), 130.32 (d, C-4), 132.48 (d, C-3′, C-7′), 134.75 (s), 135.82 (s), 136.56 (d, C-1′, C-9′), 138.34 (s), 138.41 (d, C-4′, C-6′), 140.31 (d, C-2′, C-8′), 144.86 (d, C-10′, C-11′), 145.94 (s), 153.94 (s), 187.35 (s, C-5′) ppm. MS (EI, 70 eV): *m*/*z* (%) = 348 (40) [M + 1 – BF_4]$^+$, 347 (13) [M – BF_4]$^+$, 334 (18), 331 (10), 318 (10), 207 (16), 205 (10), 196 (9), 194 (15), 193 (17), 191 (21), 179 (11), 178 (12), 131 (11), 129 (14), 117 (40), 115 (18), 105 (23), 104 (28), 103 (16), 92 (18), 91 (93), 78 (18), 77 (16), 44 (100). $C_{26}H_{19}BF_4O$ (434.24): calcd. C 71.92, H 4.41; found C 71.73, H 4.46.

5-Hydroxy-5-(1-methoxy-2-naphthyl)-5*H*-dibenzo[*a*,*d*]cycloheptene (16): 1-Methoxynaphthalene (**13**) (3.49 mL, 23.6 mmol) was added dropwise to a mixture of a 15% solution of *n*-butyllithium in *n*-hexane (16.2 mL, 25.9 mmol), additional *n*-hexane (30 mL) and TMEDA (3.88 mL, 25.9 mmol) at 0 °C. After 30 min of stirring at 40 °C, the deep-red suspension was cooled to –20 °C, and a solution of 5*H*-dibenzo[*a*,*d*]cyclohepten-5-one (5.33 g, 25 mmol) in dry diethyl ether (40 mL) was added dropwise. After stirring at room temperature for 1 d, the reaction mixture was hydrolyzed with a saturated aqueous $(NH_4)_2HPO_4$ solution (20 mL), the water layer was extracted with diethyl ether (3 × 20 mL), and the combined organic layers were dried with sodium sulfate and the solvents evaporated to dryness with a rotary evaporator. The brown crude product was purified by flash chromatography (TLC: silica; diethyl ether/*n*-hexane, 1:3; R_f = 0.38) to give 7.0 g (82%) of the tertiary alcohol **16** as colourless crystals with m.p. 187 °C (crystallized from diethyl ether/*n*-hexane, 1:2). IR (KBr): $\tilde{\nu}$ = 3061 (m), 3020 (m), 2941 (w), 2844 (w), 1931 (w, br), 1624 (w), 1594 (w), 1565 (w), 1501 (w), 1482 (m), 1434 (m), 1369 (s), 1332 (s), 1260 (m), 1226 (m), 1172 (m), 1158 (m), 1115 (m), 1086 (s), 1022 (s), 984 (m, sh), 815 (s), 796 (s), 771 (m), 752 (s), 708 (w), 665 (w) cm^{-1}. UV (acetonitrile): λ_{max} (logε) = 204 (5.23), 230 (4.93), 283 (4.27) nm. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.01 (s, 3 H), 3.77 (s, 1 H, OH), 6.67 (d, *J* = 8.8 Hz, 1 H), 6.79 (s, 2 H), 7.25 (d, *J* = 8.7 Hz, 1 H), 7.29–7.32 (m, 4 H), 7.38 ("dd", "*J*" = 6.4, 3.3 Hz, 2 H), 7.49–7.55 (m, 2 H), 7.71 ("dd", "*J*" = 6.1, 3.4 Hz, 1 H), 7.86 ("dd", "*J*" = 6.3, 3.4 Hz, 1 H), 8.22 (d, *J* = 8.0 Hz, 2 H) ppm. ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 61.68 (q), 77.99 (s, C-OH), 122.28 (d), 122.47 (d), 123.99 (d), 125.61 (d), 126.05 (d), 126.33 (d), 126.61 (d), 128.02 (d), 128.26 (d), 128.53 (d), 128.78 (s), 131.50 (d), 133.01 (s), 133.07 (s), 134.86 (s), 142.92 (s), 154.44 (s) ppm. MS (EI, 70 eV): *m*/*z* (%) = 365 (28) [M + 1]$^+$, 364 (100) [M]$^+$, 349 (10), 333 (10), 332 (10), 331 (22), 315 (12), 207 (16), 194 (14), 185 (21), 179 (14), 178 (30), 171 (10), 158 (8), 151 (9), 143 (9). $C_{26}H_{20}O_2$ (364.44): calcd. C 85.69, H 5.53; found C 85.64, H 5.59.

5-Hydroxy-5-(8-iodo-1-naphthyl)-5*H*-dibenzo[*a*,*d*]cycloheptene (18): A 15% solution of *n*-butyllithium in *n*-hexane (0.81 mL, 1.3 mmol) was added to a solution of diiodonaphthalene (500 mg, 1.32 mmol) in dry diethyl ether (20 mL) at –70 °C within 20 min. After 30 min of stirring, 5*H*-dibenzo[*a*,*d*]cyclohepten-5-one (280 mg, 1.32 mmol) in dry diethyl ether (10 mL) was added at –50 °C. The yellow solution was stirred at room temperature for 2 d. After hydrolysis with

a saturated aqueous $(NH_4)_2HPO_4$ solution (20 mL), the water layer was extracted with diethyl ether (3× 20 mL), and the combined organic layers were dried with sodium sulfate and the solvents evaporated to dryness with a rotary evaporator. The crude product (645 mg) was fractionated by flash chromatography (TLC: silica; toluene; R_f = 0.74, 0.35). **First Fraction:** 368 mg (66%) of the tertiary alcohol **18** as reddish crystals with m.p. 179 °C (crystallized from toluene). IR (KBr): $\tilde{\nu}$ = 3449 (s), 3055 (w), 3019 (w), 1626 (m, br), 1481 (w), 1434 (w), 1319 (w), 1187 (w), 1167 (w), 1156 (w), 1116 (w), 1067 (w), 1034 (m), 995 (w), 914 (w), 812 (s), 793 (m), 760 (s), 629 (m) cm^{-1}. UV (acetonitrile): λ_{max} (log ε) = 232 (4.69), 272 (4.11, sh), 296 (4.02, sh), 320 (3.84, sh) nm. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 4.73 (s, 1 H, *O*H), 5.81 (br. s, 1 H), 5.98 (br. s, 1 H), 6.89 ("d", "*J*" = 7.5 Hz, 2 H), 6.93–7.06 (br. m, 3 H), 7.17 (dt, *J* = 7.5, 1.3 Hz, 2 H), 7.39 (br. s, 1 H), 7.45 ("dd", "*J*" = 6.4, 2.9 Hz, 2 H), 7.65 (m, 2 H), 8.34 (br. m, 2 H) ppm. ^{13}C NMR (125.8 MHz, $CDCl_3$): δ = 79.42 (s), 90.04 (s), 124.43 (d), 125.28 (d), 125.85 (d), 127.48 (br. d), 128.66 (d), 128.91 (d), 132.91 (br. d), 135.34 (s), 136.77 (s), 139.27 (d), 142.88 (s) ppm. MS (EI, 70 eV): *m*/*z* (%) = 460 (5) $[M]^+$, 333 (18), 332 (30), 331 (11), 316 (12), 315 (27), 313 (16), 304 (15), 303 (40), 302 (35), 300 (18), 282 (29), 281 (100), 254 (15), 216 (14), 215 (73), 207 (13), 179 (23), 178 (63), 155 (21), 151 (12), 127 (11), 126 (16). $C_{25}H_{17}IO$ (460.31): calcd. C 65.23, H 3.27; found C 65.27, H 3.75. **Second Fraction:** 35 mg (13%) of 5*H*-dibenzo[*a*,*d*]cyclohepten-5-one as recovered starting material.

5-(8-Iodo-1-naphthyl)-5*H*-dibenzo[*a*,*d*]cyclohepten-5-ylium Tetrafluoroborate (19): HBF_4–diethyl ether (0.06 mL, 0.44 mmol) was added to the tertiary alcohol **18** (100 mg, 0.22 mmol) in dry CH_2Cl_2 (3 mL) at room temperature. After 2 min, stirring was stopped, and a layer of diethyl ether (18 mL) was carefully placed on top of the reaction mixture. After 1 d at –10 °C, the precipitate was isolated by filtration, washed with diethyl ether (2× 2 mL) and dried at room temperature/0.04 mbar to give 114 mg (99%) of the tetrafluoroborate **19** as deep-red needles with m.p. 208–212 °C. IR (KBr): $\tilde{\nu}$ = 3042 (w), 3011 (w), 1602 (w), 1516 (w), 1432 (m), 1388 (s), 1337 (w), 1194 (w), 1124 (m), 1084 (s, br), 814 (w), 765 (w), 733 (w) cm^{-1}. UV (acetonitrile): λ_{max} (log ε) = 233 (4.65), 310 (4.75), 383 (3.72), 421 (3.61), 566 (3.55, sh) nm. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.36 ("dd", "*J*" = 8.1, 7.5 Hz, 1 H, 6-H), 7.49 (dd, *J* = 7.2, 1.2 Hz, 1 H, 2-H), 7.78 ("dd", "*J*" = 8.1, 7.3 Hz, 1 H, 3-H), 7.99 ("ddd", "*J*" = 8.6, 5.5, 1.4 Hz, 2 H, 3′-H, 7′-H), 8.08 (1 H, 7-H), 8.09 (2 H, 4′-H, 6′-H), 8.26 (dd, *J* = 8.3, 1.0 Hz, 1 H, 5-H), 8.34 (dd, *J* = 8.2, 1.2 Hz, 1 H, 4-H), 8.53 ("ddd", "*J*" = 8.1, 5.7, 1.1 Hz, 2 H, 2′-H, 8′-H), 8.84 (dd, *J* = 8.3, 1.1 Hz, 2 H, 1′-H, 9′-H), 9.47 (s, 2 H, 10′-H, 11′-H) ppm. ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 91.59 (s, C-8), 125.23 (d, C-3), 128.92 (d, C-6), 131.06 (d, C-5), 131.84 (s), 132.54 (d, C-4), 133.01 (d, C-2), 133.12 (d, C-3′, C-7′), 135.65 (s), 136.79 (d, C-1′, C-9′), 138.22 (d, C-4′, C-6′), 138.37 (s), 140.40 (d, C-2′, C-8′), 141.42 (s), 143.02 (d, C-7), 145.72 (s), 146.33 (d, C-10′, C-11′), 182.17 (s, C-5′) ppm. MS (EI, 70 eV): *m*/*z* (%) = 443 (31) $[M + 1 - BF_4]^+$, 442 (96), 316 (31), 315 (84), 314 (54), 313 (100), 312 (11), 311 (28), 300 (15), 158 (27), 157 (27), 157 (34). $C_{25}H_{16}BF_4I$ (530.11): calcd. C 56.64, H 3.04; found C 56.68, H 3.07.

5*H*,2′*H*-Spiro[dibenzo[*a*,*d*]cycloheptene-5,2′-naphtho[1,8-*bc*]furan] (4c): A suspension of tertiary alcohol **18** (459 mg, 1.00 mmol) and NaH (120 mg, 3.00 mmol, 60% in mineral oil) in dry THF (30 mL) was heated under reflux for 1 d. After hydrolysis with a saturated aqueous $(NH_4)_2HPO_4$ solution (20 mL), the water layer was extracted with diethyl ether (3× 20 mL), and the combined organic layers were dried with sodium sulfate and the solvents evaporated to dryness with a rotary evaporator. Column chromatography (silica; toluene) of the residue resulted in 117 mg (32%) of the naphthofuran **4c** as colourless needles with m.p. 171 °C (from dichloromethane/*n*-hexane, 1:3). IR (KBr): $\tilde{\nu}$ = 3063 (w), 3024 (w), 1633 (m), 1615 (m), 1587 (s), 1491 (s), 1463 (m), 1434 (w), 1370 (s), 1252 (s), 1224 (m), 1174 (w), 1117 (m), 946 (s), 885 (w), 809 (s), 798 (s), 767 (s), 730 (m) cm^{-1}. UV (acetonitrile): λ_{max} (log ε) = 217 (4.65), 243 (4.49), 304 (4.20), 328 (3.95, sh) nm. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 6.94 (d, *J* = 7.3 Hz, 1 H, 7-H), 7.20 (s, 2 H, 10′-H, 11′-H), 7.24 (d, *J* = 8.1 Hz, 1 H, 5-H), 7.25–7.32 (m, 4 H, 2′-H, 3′-H, 7′-H, 8′-H), 7.36 ("dd", "*J*" = 8.1, 7.2 Hz, 1 H, 3-H), 7.42 (1 H, 6-H), 7.43 (dd, *J* = 7.2, 1.3 Hz, 2 H, 4′-H, 6′-H), 7.60 (d, *J* = 8.0 Hz, 1 H, 4-H), 8.00 (d, *J* = 7.1 Hz, 1 H, 2-H), 8.01 (dd, *J* = 7.8, 1.5 Hz, 2 H, 1′-H, 9′-H) ppm. ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 96.25 (s, C-5′), 100.94 (d, C-7), 116.07 (d, C-5), 119.45 (d, C-2), 124.35 (d, C-4), 125.05 (d, C-1′, C-9′), 126.19 (s), 127.58 (d), 128.42 (d, C-3), 128.87 (d), 129.34 (d, C-6), 130.40 (d, C-4′, C-6′), 132.07 (s), 132.73 (d, C-10′, C-11′), 132.93 (s), 139.53 (s), 144.17 (s), 158.34 (s, C-8) ppm. MS (EI, 70 eV): *m*/*z* (%) = 333 (30) $[M + 1]^+$, 332 (100) $[M]^+$, 331 (99), 330 (5), 329 (10), 313 (7), 303 (8), 302 (16), 301 (7), 300 (13), 252 (7), 178 (6), 166 (10), 155 (6), 152 (8), 151 (10), 144 (7), 126 (14). $C_{25}H_{16}O$ (332.40): calcd. C 90.34, H 4.85; found C 90.33, H 4.86.

NMR Experiment. 5-(8-Hydroxy-1-naphthyl)-5*H*-dibenzo[*a*,*d*]cyclohepten-5-ylium Trifluoromethanesulfonate (6c): Trifluoromethanesulfonic acid (6.7 μL, 11.5 mg, 0.075 mmol) was added to naphthofuran **4c** (22 mg, 0.068 mmol) in $CDCl_3$ (0.7 mL) in an NMR tube at room temperature. The deep-violet solution was homogenized in a sonicator. The ^{1}H NMR spectrum showed exclusively one data set that was in accord with the cycloheptenylium salt **6c**. ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 6.75 (br. s, 1 H), 7.25 (br. "d", "*J*" = 5.0 Hz, 1 H), 7.57 (br. s, 1 H), 7.77 (br. s, 2 H), 8.01 ("t", "*J*" = 7.7 Hz, 2 H, 3′-H, 7′-H), 8.26 (d, *J* = 8.1 Hz, 1 H), 8.31 (d, *J* = 8.7 Hz, 2 H, 4′-H, 6′-H), 8.51 ("t", "*J*" = 7.7 Hz, 2 H, 2′-H, 8′-H), 8.71 (d, *J* = 8.1 Hz, 2 H, 1′-H, 9′-H), 9.10 (s, 2 H, 10′-H, 11′-H) ppm.

X-ray Structure Determinations: Crystallographic data were collected with a Siemens P4RA diffractometer, equipped with a rotating anode (**4a**) and with a conventional Siemens P4 diffractometer (**19**). Graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å) was used in both cases. Data sets were collected at *T* = 150 (**4a**) and 293(2) K (**19**). Empirical absorption corrections based on ψ scans were applied to both data sets. The structures were solved by direct methods and refined with full-matrix least-squares techniques against F^2 (SHELXL-97).[17] The positions of the hydrogen atoms were calculated by assuming idealized geometries and were refined by using riding models. **4a:** $C_{28}H_{20}N_2O_2$, *M* = 416.46 g mol^{-1}, triclinic, space group $P\bar{1}$ (No. 2), *a* = 10.091(1), *b* = 11.121(1), *c* = 19.396(2) Å, α = 88.49(1), β = 85.21(1), γ = 80.54°, *V* = 2139 Å^3, *Z* = 4, D_x = 1.293 g cm^{-3}, μ(Mo-K_α) = 0.080 mm^{-1}, transmission range 0.953–0.821, $2\theta_{max}$ = 54°, ω scans, crystal dimensions approx. 0.26× 0.19× 0.17 mm, 9224 unique reflections, R_1 (wR_2) = 0.0391 (0.0978), 580 variables. **19:** $C_{25}H_{16}BF_4I$, *M* = 530.09 g mol^{-1}, monoclinic, space group *C*2/*c* (No. 15), *a* = 28.995(5), *b* = 8.220(1), *c* = 22.340(4) Å, β = 128.95(1)°, *V* = 4141 Å^3, *Z* = 8, D_x = 1.701 g cm^{-3}, μ(Mo-K_α) = 1.592 mm^{-1}, transmission range 0.970–0.774, $2\theta_{max}$ = 50°, ω scans, crystal dimensions approx. 0.52× 0.33× 0.30 mm, 3316 unique reflections, R_1 (wR_2) = 0.0733 (0.1510), 281 variables.

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