Reactions of Benzocycloheptenes with Dienophiles

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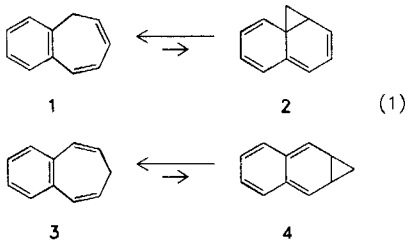
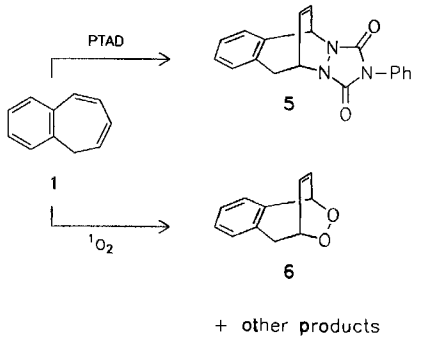
The Diels-Alder reactions of 5*H*-benzocycloheptene (**1**) with tetracyanoethylene (TCNE) afforded the [2 + 2] and [4 + 2] cycloadducts **7**, **8**, and **10** and the benzodicyanoheptafulvalene **9**. The norcaradiene product **10** was synthesized independently by cycloaddition of TCNE to 7*H*-benzocycloheptene (**3**). The addition of 4-methyl-1,2,4-triazoline-3,5-dione (MTAD) to **3** gave bis-urazole **13**, which was formed by ene reaction followed by [4 + 2] cycloaddition. The spirocycloheptatriene **15** gave with 4-phenyl-1,2,4-triazoline-3,5-dione (PTAD) the bis-urazole **16**.

Cycloheptatriene can undergo two dynamic processes, namely ring inversion and valence isomerization[1]. The valence isomers of cycloheptatriene, namely tropylidene and norcaradiene, have been detected by dynamic ^{1}H-NMR spectroscopy[2] for a few 7-substituted cycloheptatrienes, but the parent norcaradiene has not been observed so far[3]. These two dynamic processes make cycloheptatriene and its derivatives intriguing compounds in view of their diverse Diels-Alder reaction modes. We[4] and others[5] have shown, that cycloheptatriene can undergo all possible Diels-Alder reactions, forming products arising from [2 + 2], [4 + 2], and [6 + 2] addition to tropylidene and [4 + 2] addition to norcaradiene. However, if one of the double bonds of the cycloheptatriene is part of a benzene ring, only the triene form is found. Therefore, since norcaradiene valence isomers **2** and **4** of benzocycloheptenes **1** and **3** would involve the formation of quinoid from benzoid rings, it is not surprising that these are not directly observed (Eq. 1).



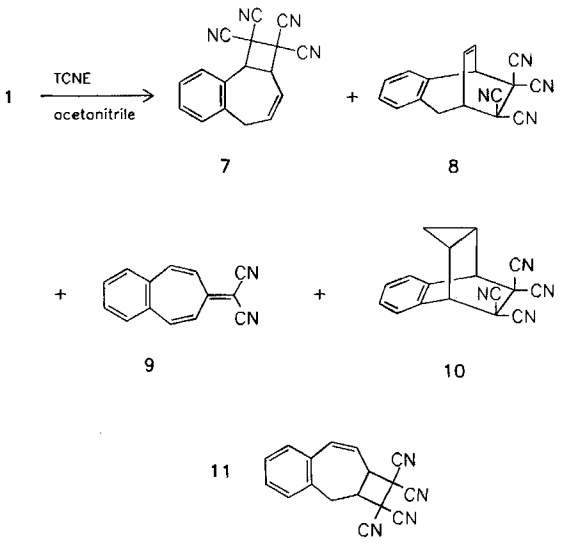
(1)

Recently, we reported[6] that 5*H*-benzocycloheptene (**1**) with 4-phenyl-1,2,4-triazoline-3,5-dione (PTAD) at ambient temperature gave the [4 + 2] cycloadduct **5** as the sole product. However, the reaction of **1** with singlet oxygen led to a complex product mixture, which consisted of the expected endoperoxide **6** as well as α-naphthaldehyde and open-chain aldehydes (Eq. 2). In this communication we present unusual results on the cycloaddition of tetracyanoethylene and triazolinedione to the benzocycloheptenes **1** and **3** and related systems.



(2)

A mixture of cycloheptatriene **1** and tetracyanoethylene in acetonitrile was allowed to react at ambient temperature for eight days. The reaction led to a complex product mixture as attested by ^{1}H-NMR analysis of the crude product mixture, with the [2 + 2] cycloadduct **7** as the major product (Eq. 3). Attempted isolation of **7** failed due to decomposition during column chromatography. However, we were able to extract the ^{1}H-NMR data of **7** directly from the crude prod-



(3)

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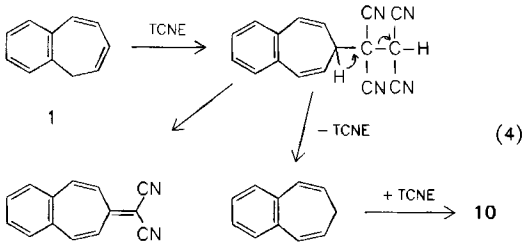
uct mixture and to assign its structure excluding the other possible cycloaddition product **11**.

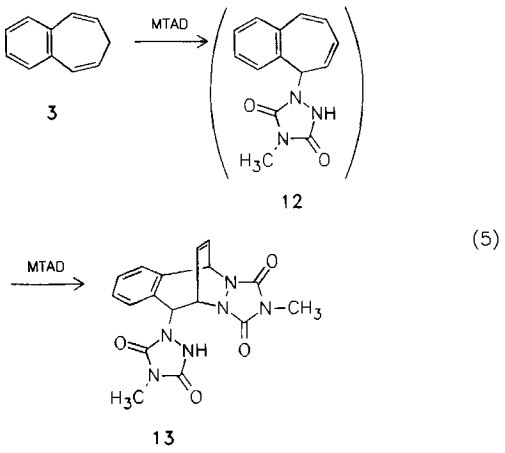
As the first fraction of the silica gel column chromatography a mixture of **8** and **10** in the ratio of 73:27 was isolated in 4% yield. The last fraction afforded the known[7] benzodicyanoheptafulvalene **9**, also in a yield of 4%. The structure of **8** was established by comparison of its NMR spectrum with the spectra of **5** and **6**. While **7** and **8** are the expected products arising from [2 + 2] and [4 + 2] cycloaddition of TCNE to **1**, the heptafulvalene **9** and the norcaradiene adduct **10** were unusual. A rationalization for the formation of the norcaradiene adduct **10** is to assume a TCNE-catalyzed isomerization of benzocycloheptene **1** into its regioisomer **3**, followed by [4 + 2] cycloaddition (Eq. 4).



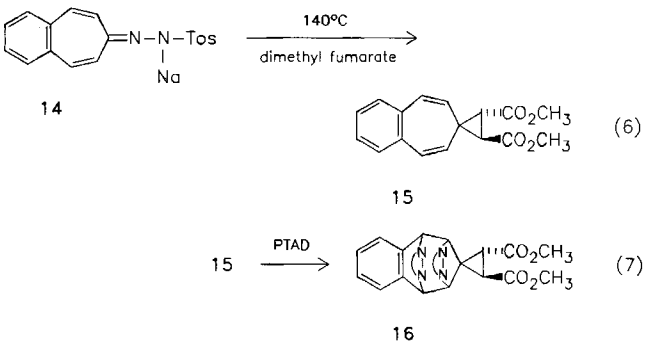
In order to confirm this mechanism, we studied the cycloaddition of authentic benzocycloheptene **3** with TCNE independently. A mixture consisting of TCNE and **3** in acetonitrile was stirred at room temperature for 22 hours. After flash chromatography, the cycloadduct **10** was isolated in 27% yield as the sole product. The spectral data of **10** were in accord with those obtained in the reaction of TCNE with **1**, which corroborates our mechanistic suggestion in Eq. (4). The question whether **10** was formed by cycloaddition of TCNE to the valence isomer norcaradiene or by direct cycloaddition of TCNE to **3** (homo-Diels-Alder reaction) cannot be answered on the basis of the present data; however, recently Balci et al.[8] and Leitich et al.[9] have also shown that benzocycloheptene derivatives can form norcaradiene-type cycloaddition products.

Of interest in this context is the reaction of benzocycloheptene **3** with 4-methyl-1,2,4-triazoline-3,5-dione (MTAD), leading to the bis-urazole **13** (Eq. 5). A solution of **3** in dichloromethane was treated with 2 mol of MTAD at –30°C, and after flash chromatography the double adduct **13** was isolated as colorless solid. ^{1}H- and ^{13}C-NMR data and especially elemental analysis indicated the incorporation of two mol of MTAD. At first, cycloaddition of one mol of MTAD afforded the ene product **12**, followed by a [4 + 2] cycloaddition of another mol of MTAD to give the 1,3-diene moiety.

In order to prevent the ene reaction, it was decided to block the 7,7-position in the benzocycloheptene **3** by means of a cyclopropane ring. For this purpose spirocyclopropane derivative **15** was prepared by addition of benzocycloheptenylidene to dimethyl fumarate, the latter being generated by thermolysis of the tosyl hydrazone **14** (Eq. 6). Temperatures in the range of 130°C were required to effect the thermal decomposition of the tosyl hydrazone salt[10].



Contrary to the observation by Jones et al.[10], we obtained the corresponding spirocyclopropane **15** in 14% yield. The structure of **15** was established unambiguously on the basis of ^{1}H- and ^{13}C-NMR spectra. The AB pattern arising from the olefinic protons supports the proposed assignment, while the nine-line ^{13}C-NMR spectrum speaks for the symmetrical structure.



Treatment of **15** with PTAD in dichloromethane at ambient temperature afforded the cycloadduct **16** in 16% yield. The structure of the double adduct **16** was determined on the basis of ^{1}H- and ^{13}C-NMR spectral data. The bridgehead protons give rise to separated AB patterns at δ = 5.0–6.1, the cyclopropane protons resonate as an AB system at δ = 2.45 and 3.3. The methoxy protons give rise to two singlets at δ = 3.45 and 3.7 as expected according to the unsymmetrical geometry of these groups. The bis-urazole **16** was presumably formed by cycloaddition of one mol of PTAD to the cycloheptatriene unit, which resulted in an *ortho*-quinoid structure that was trapped readily by a second mol of PTAD.

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Experimental

Melting points (uncorrected): Reichert Thermovar Kofler apparatus. – IR: Beckman Acculab 4 or Perkin Elmer 377. – ^{1}H NMR: Hitachi-Perkin-Elmer R 24 B (60 MHz), EM 360 Varian (60 MHz), or Bruker WM 200 (200 MHz), TMS internal stand-

ard. – ^{13}C NMR: Bruker WM 200 (50.3 MHz), $CDCl_3$ internal standard. Column chromatography: silica gel (70–230 mesh ASTM, activity III), alumina (neutral, activity III), adsorbent-substrate ratio of ca. 100:1. – The benzocycloheptenes **1** and **3** were synthesized as described in the literature[11].

Cycloaddition of TCNE to 5H-Benzocycloheptene (**1**): To a solution of 994 mg (7.00 mmol) of **1** in 10 ml of dry acetonitrile was added a solution of 894 mg (7.00 mmol) of TCNE at 20°C. The brown reaction mixture was stirred at room temp. for 8 d, the solvent roto-evaporated and the residue flash-chromatographed on silica gel at −10°C by eluting with dichloromethane. A mixture (84 mg, 4%) of cycloadducts **8** and **10** (73:27) was collected as the first fraction (R_f = 0.63). The second fraction (R_f = 0.59) gave 96 mg of the known[7] heptafulvalene **9** as yellow powder. Crystallization from ethanol gave 60 mg (4%) of **9** as yellow needles, m.p. 264–265°C (ref.[7] 264–265°C). The remainder consisted of undefined, higher-molecular-mass products, which were retained on the silica gel column. Attempts to isolate pure cycloadducts 7 and **8** failed, so that no analytical data could be obtained and only pertinent spectral data are given. Pure cycloadduct **10** was isolated from the reaction of TCNE with benzocycloheptene **3** (see below).

2,3-Benzo-8,8,9,9-tetracyanobicyclo[5.2.9]nona-2,5-diene (7): ^1H NMR (CD_3CN, 200 MHz): δ = 4.26 (ddd, $J_{7,1}$ = 4.3, $J_{7,6}$ = 4.3, $J_{7,5}$ = 1.5 Hz, 1H, 7-H), 5.01 (d, $J_{4,5}$ = 8.7 Hz, 2H, 4-H), 5.20 (dd, $J_{1,6}$ = 1.7, $J_{1,7}$ = 4.3 Hz, 1H, 1-H), 6.32 (ddd, $J_{6,5}$ = 11.0, $J_{6,7}$ = 4.3, $J_{6,1}$ = 1.7 Hz, 1H, 6-H), 6.82 (ddd, $J_{5,6}$ = 11.0, $J_{5,4}$ = 8.7, $J_{5,7}$ = 1.5 Hz, 1H, 5-H), 7.4–8.0 (m, aromatic H).

2,3-Benzo-8,8,9,9-tetracyanobicyclo[3.2.2]nona-2,6-diene (**8**): ^1H NMR (CD_3CN, 200 MHz): δ = 3.26 (AB system, d, B part, J_{AB} = $J_{4,4'}$ = 19.0, $J_{4',5}$ = 3.5 Hz, 1H, 4′-H), 3.59 (AB system, d, A part, J_{AB} = $J_{4,4'}$ = 19.0 Hz, 1H, 4-H), 3.82 (dddd, $J_{5,4}$ = 4.0, $J_{5,4'}$ = 3.5, $J_{5,9}$ = 7.5 Hz, 1H, 5-H), 4.46 (dd, $J_{1,8}$ = 7.5, $J_{1,9}$ = 0.6 Hz, 1H, 1-H), 6.59 (ddd, $J_{1,9}$ = 0.6, $J_{9,5}$ = 7.5, $J_{8,9}$ = 8.8 Hz, 1H, 9-H), 6.79 (ddd, $J_{8,1}$ = 7.5, $J_{8,5}$ = 1.0, $J_{8,9}$ = 8.8 Hz, 1H, 8-H), 7.1–7.5 (m, aromatic H).

3,4-Benzo-8,8-dicyanoheptalene (**9**)[7]: IR (KBr): $\tilde{\nu}$ = 2210 cm^{-1} (CN), 1630, 1555, 1490, 1418, 1350, 1270, 1175, 842, 765. – ^1H NMR ($CDCl_3$, 200 MHz): δ = 7.18 (AB system, dd, B part, J_{AB} = $J_{1,2}$ = $J_{5,6}$ = 12.1, J = 1.0, J = 1.0 Hz, 2H, 1,6-H), 7.30 (AB system, dd, A part, J_{AB} = $J_{1,2}$ = $J_{5,6}$ = 12.1, J = 1.0, J = 1.0 Hz, 2H, 2,5-H), 7.62 (br. s, 4H, aromatic H). – ^{13}C NMR ($CDCl_3$, 50 MHz): δ = 74.9 (s, C-8), 114.2 (s, CN), 127.8 (d), 131.8 (d), 134.5 (d), 137.7 (s, C-3,4), 143.2 (d), 161.6 (s, C-7). – MS (70 eV): *m/z* (%) = 204 (100) [M^+], 178 (10), 177 (32), 176 (11), 151 (7), 150 (7), 115 (18), 102 (6), 89 (4), 75 (9), 63 (7).

6,7-Benzo-9,9,10,10-tetracyanotricyclo[3.2.2.0^{2,4}]non-8-ene (**10**) was identified as the cycloadduct isolated in the reaction of benzocycloheptene **3** with TCNE (see below).

Cycloadduct **10** *by Reaction of 7H-benzocycloheptene* (**3**) *with TCNE:* To a solution of 640 mg (5.00 mmol) of TCNE in 10 ml of acetonitrile was added a solution of 568 mg (4.00 mmol) of **3** in 5 ml of acetonitrile at ambient temperature. The resulting solution was stirred at room temp. for 22 h. The solvent was evaporated at reduced pressure and the residue flash-chromatographed on 200 g of silica gel by eluting with dichloromethane (R_f = 0.65). The yellow fraction was collected, and after evaporation of the solvent the product was crystallized from ethanol. Repeated recrystallization from ethanol gave 253 mg (27%) of cycloadduct **10**, m.p. 223–224°C. – IR (KBr): $\tilde{\nu}$ = 3060 cm^{-1}, 2250 (CN), 2210 (CN), 1625, 1550, 1482, 1412, 1372, 1325, 1265, 1210, 1108, 1092, 1072, 1055, 1030, 880, 770, 725, 657. – ^1H NMR ([D_6] acetone, 200 MHz): δ = −0.56 (dt, $J_{3n,2}$ = $J_{3n,4}$ = 3.7, $J_{3n,3x}$ = 6.2 Hz, 1H, 3-H_n), 0.75 (dt, $J_{3x,2}$ = $J_{3x,4}$ = 7.7, $J_{3x,3n}$ = 6.2 Hz, 1H, 3-H_x), 1.92 (m, 2H, 2,4-H), 4.77 (m, 2H, 1,5-H), 7.4–7.6 (m, 4H, aromatic H). – ^{13}C NMR ([D_6] acetone, 50 MHz): δ = 6.5 (t, C-3), 7.8 (d, C-2,4), 45.0 (s, C-6,7), 46.3 (d, C-1,5), 112.8 and 112.9 (two s, CN), 128.1 and 131.0 (two d, C aromatic), 132.9 (s, C-8,9). – MS (70 eV): *m/z* (%) = 270 (0.05) [M^+], 204 (17), 143 (12), 142 (100, M − TCNE), 141 (36), 140 (6), 139 (5), 115 (25), 9 (4).

$C_{17}H_{10}N_4$ (270.3) Calcd. C 75.54 H 3.73 N 20.73
Found C 75.71 H 3.67 N 20.06

Cycloadduct **13** *by the Reaction of 7H-Benzocycloheptene* (**3**) *with 4-Methyl-1,2,4-triazoline-3,5-dione:* To a stirred solution of 213 mg (1.50 mmol) of **3** in 5 ml of dichloromethane was added at 25°C in small portions 339 mg (3.00 mmol) of MTAD. After allowing the reaction mixture to come to room temp, (ca. 20°C), it was stirred for 30 min and the solvent evaporated at reduced pressure (ca. 20°C at 15 Torr). Flash chromatography with ethyl acetate/acetone (10:1) as eluant on silica gel gave 460 mg of cycloadduct **13** as yellow powder (R_f = 0.39). Repeated recrystallization from ethanol gave 303 mg (55%) of a colorless powder, m.p. 159–160°C. – IR (KBr): $\tilde{\nu}$ = 3460 cm^{-1} (NH), 1760 (C=O), 1465, 1395, 1220, 1025, 960, 860, 770, 695. – ^1H NMR ($CDCl_3$, 200 MHz): δ = 3.02 (s, 3H, NCH_3), 3.08 (s, 3H, NCH_3), 5.25 (ddd, $J_{1,2}$ = 4.2, $J_{1,8}$ = 6.6, $J_{1,9}$ = 1.0 Hz, 1H, 1-H), 5.55 (d, $J_{5,9}$ = 6.6 Hz, 1H, 5-H), 5.76 (d, $J_{2,1}$ = 4.2 Hz, 1H, 2-H), 6.23 (ddd, $J_{9,1}$ = 1.0, $J_{9,5}$ = 6.6, $J_{9,8}$ = 8.7 Hz, 1H, 9-H), 6.76 (ddd, $J_{8,1}$ = 6.6, $J_{8,9}$ = 8.7, $J_{8,5}$ = 1.0 Hz, 1H, 8-H), 7.1–7.5 (m, 4H, aromatic H), 8.0 (br. s, 1H, NH). – ^{13}C NMR ($CDCl_3$, 50 MHz): δ = 25.4 (q, NCH_3), 25.7 (q, NCH_3), 52.8, 55.8, 57.1 (d, C-1,2,5), 124.5 (d), 128.7 (d), 128.9 (d), 129.7 (d), 130.8 (d), 131.7 (s), 134.8 (d), 135.1 (s), 153.4, 153.4, 153.9, 154.5 (s, 4 C=O). – MS (70 eV): *m/z* (%) = 368 (3) [M^+], 254 (41), 253 (100), 197 (31), 169 (20), 168 (40), 155 (10), 154 (39), 152 (12), 142 (17), 141 (62), 128 (23), 127 (22), 59 (49).

$C_{17}H_{16}N_6O_4$ (368.4) Calcd. C 55.41 H 4.38 N 22.81
Found C 55.47 H 4.47 N 22.50

Sodium Salt of 4,5-Benzotropone Tosylhydrazone[10] (**14**): To a solution of 1.00 g (3.09 mmol) of 4,5-benzotropone tosylhydrazone in 20 ml of THF was added 98 mg (4.09 mmol) of NaH at room temp., which resulted in evolution of hydrogen concomitant with precipitation of a red orange solid. After stirring for 1 h, 50 ml of dry pentane was added and the solution filtered. The sodium salt **14** (1.18 g, 98%) was dried over P_2O_5 at reduced pressure, and a bright yellow solid, that decomposed at 130°C with gas evolution, was obtained.

Spirocycloheptatriene **15** *by Thermolysis of* **14** *in the Presence of Dimethyl Fumarate:* To a solution of 1.46 g (10.0 mmol) dimethyl fumarate in 30 ml of dry xylene was added 250 mg (0.720 mmol) of salt **14** under nitrogen. The reaction mixture was maintained at ca. 140°C for 6.5 h, cooled to room temp. (ca. 20°C), and poured into 100 ml of water. The aqueous solution was extracted several times with dichloromethane, the combined organic phases were washed with water and dried with magnesium sulfate. The solvent was roto-evaporated and the residue taken up in ether, and part of the dimethyl fumarate precipitated. The residue was submitted to column chromatography on alumina (neutral, activity III) by eluting with ether/petroleum ether (1:5). Dimethyl fumarate was collected as the first fraction. The second fraction (yellow band) gave the expected spirocycloheptatriene **15**. Additional column chromatography and crystallization of the crude product from chloroform gave an analytically pure sample of 29 mg (14%) of yellow solid **15**, m.p. 69–70°C. – IR ($CHCl_3$): $\tilde{\nu}$ = 3020 cm^{-1}, 1720 (C=O), 1160, 1355. – ^1H NMR ($CDCl_3$, 60 MHz): δ = 2.4 (s, 2H,

cyclopropane H), 3.65 (s, 6H, CH_3), 5.4 (d, J = 11.2 Hz, B part of AB system, 2H, 2,7-H), 6.7 (d, J = 11.2 Hz, A part of AB system, 2H, 3,6-H), 7.2 (s, 4H, aromatic H). – ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 36.5 (s, cyclopropane), 36.8 (d, cyclopropane), 52.1 (q, CH_3), 127.1 (d), 128.4 (d), 130.7 (d), 132.8 (d), 135.9 (s), 169.0 (s, C=O). – MS (70 eV): m/z (%) = 284 (13) [M^+], 253 (6.8), 225 (100), 211 (3.7), 181 (4.1), 166 (21.5), 165 (73), 139 (21), 115 (12.7), 82 (28.4).

$C_{17}H_{16}O_6$ (284.4) Calcd. C 71.81 H 5.67
Found C 71.72 H 5.77

Cycloadduct **16** *by Reaction of 4-Phenyl-1,2,4-triazoline-3,5-dione with Spirocycloheptatriene* **15**: To a stirred solution of 100 mg (0.35 mmol) of **15** in 30 ml of dichloromethane was added at room temp. in small portions 123 mg (0.700 mmol) of PTAD within 30 min and the mixture stirred at the same temp. for 6 h. After evaporation of the solvent, the residue was submitted to column chromatography on alumina (neutral, activity III) by eluting with petroleum ether/ethyl acetate (1:1). As the first fraction the starting material was collected. The second fraction gave 74 mg (16%) of the cycloadduct **16** as white solid, m. p. 208–209°C (from chloroform). – IR (KBr): $\tilde{\nu}$ = 1720 cm^{-1} (C=O), 1390, 1350, 1250, 1175, 1150, 1000, 930, 890, 770. – ^{1}H NMR ($CDCl_3$, 60 MHz): δ = 2.45 (AB system, d, B part, 1H, cyclopropane H), 3.3 (AB system, d, A part, 1H, cyclopropane H), 3.45 (s, 3H, CH_3), 3.70 (s, 3H, CH_3), 5.0–6.1 (2 AB systems, 4H, NCH–), 7.3 (br. s, 14H, aromatic H). – ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 29.1, 29.7, 47.56, 53,4, 53.4, 58,0, 58.1, 59.9, 62.8, 125.4, 125.7, 127.1, 127.2, 128.5, 128.7, 129.2, 129.5, 129.6, 130.8, 131.0, 132.1, 132.2, 152.0, 152.1, 155.5, 155.7, 168.0, 169.5. – MS (70 eV): m/z (%) 542 (1), 472 (1), 458 (45), 357 (10.8), 356 (41.5), 299 (15), 298 (86.8), 285 (36.6), 277 (16), 179 (43.5), 152 (16), 147 (27.5), 130 (95.8), 103 (100).

$C_{33}H_{26}N_6O_8$ (634.6) Calcd. C 62.45 H 4.12 N 13.24
Found C 62.34 H 4.19 N 13.09

CAS Registry Numbers

1: 264-08-4 / **3**: 264-09-5 / **7**: 128871-01-2 / **8**: 128871-02-3 / **9**: 39665-72-0 / **10**: 128871-03-4 / **13**: 128871-04-5 / **15**: 128870-99-5 / **16**: 128871-00-1 / TCNE: 670-54-2 / 4,5-benzotropone tosylhydrazone: 40154-60-7 / 4-methyl-1,2,4-triazoline-3,5-dione: 16312-79-1 / dimethyl fumarate: 624-49-7

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