Reaction of Herz salts with malononitrile: a general route to (6H-1,2,3-benzodithiazol-6-ylidene)malononitriles

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The term “Herz reaction” describes the condensation of aromatic amines and disulfur dichloride to give the corresponding 1,2,3-benzodithiazolium chlorides (Herz salts) and their subsequent hydrolysis to afford 2-aminobenzenethiols.1,2 This transformation and the accompanying para-chlorination of the starting amine have received considerable attention.3 However, although 1,2,3-benzodithiazolium salts have been known for 80 years, their chemistry that does not involve degradation of the heterocyclic ring is still surprisingly sparse.

Recently we needed an independent synthesis of (5H-naphtho[1,2-d][1,2,3]dithiazol-5-ylidene)malononitrile 2i and were able to prepare it from 1-aminonaphthalene, which gave 5-chloronaphtho[1,2-d][1,2,3]dithiazolium chloride when treated with disulfur dichloride; when this Herz compound was treated with malononitrile and base (Scheme 1). The mixture reaction with malononitrile and base (Scheme 1). The mixture

6-Chloro-1,2,3-benzodithiazolium chlorides 1 (Herz salts) react with malononitrile to afford the highly coloured ylidenes 2 in low to moderate yields. The reaction is general but complex and in the case of the 6-chloro-4-methoxy-1,2,3-benzodithiazolium chloride 1e the by-products 6-chloro-4-methoxy-1,3-benzothiazole-2-carbonitrile 3, 6-chloro-4-methoxy-2,3-di-hydro-1,3-benzothiazole-2,2-dicarbonitrile 4, and 4-methoxy-6-thiocyanato-1,3-benzothiazole-2-carbonitrile 5 were also isolated.

The reactions were complex (TLC) but the ylidenes could be readily identified by their intense blue–lilac colour in solution; any co-running by-products could be removed from the chromatographed fraction containing the ylidene by one or two recrystallisations from glacial acetic acid. The naphtho- and the 1,2,5-benzothiadiazza Herz salts gave the best yields (40 and 30% respectively) and it is presumed that the stability added by the fused aromatic ring is the contributing factor.

Interestingly the reaction of 3-monosubstituted anilines with S2Cl2 to form Herz salts was reported to result in cyclisation exclusively para to that substituent.6 Whilst 3-methoxylaniline followed this trend, the Herz salts 1c and 1d derived from 3-methylaniline gave a mixture of 5-methyl (2c) and the more sterically demanding 7-methyl substituted ylidene (2d) upon reaction with malononitrile and base (Scheme 1). The mixture

was inseparable but the 1H and 13C NMR data for the condensation products 2c and 2d confirmed their identity. The ratio of 2c : 2d was 2 : 1 (by 1H NMR) after recrystallisation from glacial acetic acid.

In the solid state the ylidenes 2 were lustrous and metallic in appearance. In solution the compounds were deep blue or lilac in colour, with the lowest energy UV absorption bands as high as \( \lambda_{\text{max}} \) 575 nm (log \( \epsilon \) 4.35). This transition shifts further into the red with increasing solvent polarity which suggests intramolecular charge transfer. The 1H NMR data of ylidenes 2

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indicated that a considerable negative charge was located on the central carbon of the malononitrile group [60–63 ppm, C(CN)$_2$] indicating the presence of a considerable push–pull effect, the ‘push’ originating presumably from both sulfurs in the dithiazole ring.

Despite attempts to optimise conditions for the treatment of the Herz salts with malononitrile to give the ylidenes, the yields were poor; variables investigated were reaction time, rate of addition of base, quantity of base, order of addition, reaction solvent (DCM, THF, EtOH) and base (Hüg’s base, pyridine, DBU). The only factor that significantly affected the yields of the ylidenes 2 was the quantity of base. If less base was added the yield dropped; a 2 : 1 stoichiometry of base to malononitrile was optimal.

The other products formed during the ylidene synthesis from 4-methoxy-1,2,3-benzodithiazolium chloride 1e and malononitrile in the presence of Hüg’s base were investigated. Apart from the ylidene 2e (11%), three other compounds were isolated. A fluorescent cream coloured solid was identified as 6-chloro-4-methoxybenzothiazole-2-carbonitrile 3 (24%); a $^1$H–$^{13}$C correlation $^{13}$C NMR eliminated the possibility of the isomeric benzothiazole structure. A trace amount of a faint yellow crystalline compound 4 was isolated and tentatively assigned the dicyanomethylene structure, based on the LRMS and on the fact that it readily formed the benzothiazole 3 on standing. The remaining compound was tentatively assigned as 4-methoxy-6-thiocyanatobenzothiazole-2-carbonitrile 5 (5%).

All the standard spectral data were collected for the compound 5 which is isomeric with the ylidene 2e, C$_{16}$H$_{11}$N$_3$Os$_2$, as shown by microanalysis and HRMS. However compound 5 is almost colourless and does not show the typical ylidene absorptions in the UV spectrum; its spectrum $\lambda_{max}$ 303 (log $\varepsilon$ 4.06) and 344 nm (3.84) was very similar to that of the benzothiazole 3 $\lambda_{max}$ 302 (log $\varepsilon$ 4.17) and 339 nm (3.78), and both compounds were strongly fluorescent. The LRMS of compound 5 had a relatively intense fragmentation from the parent ion $\text{m/z}$ (EI) 247 (62%) to 218 (100) which was significantly absent in the LRMS of the ylidene 2e. LSMS confirmed the fragment $\text{m/z}$ (EI) 218 (100%) to come directly from the parent ion. A similar fragmentation was seen from the benzothiazole 3 parent ion $\text{m/z}$ (EI) 224 (54%) to 195 (100). HRMS supported the formula of CHO for this fragment. The IR data show two very different nitrite stretches for 5 at 2231 and 2159 cm$^{-1}$ and the low wavenumber nitrite stretch is in the region for thiocyanates (2170–2135 cm$^{-1}$). The $^{13}$C NMR shows ten separate carbon environments, two of which can be identified as belonging to the two nitriles (112.9 and 109.7 ppm) and one of which is the methoxy carbon resonance (57.3 ppm). The $^1$H NMR shows the same aromatic substitution pattern as for the benzothiazole 3 and the ylidene 2e. Like the UV data, the $^{13}$C and $^1$H NMR patterns for the aromatic resonances were closer to the benzothiazole 3 than to the ylidene 2e. Based on all this we have assigned the compound as the 6-thiocyanato derivative 5.

A suspicion that 6-chloro-4-methoxy-1,2,3-benzodithiazole 2-oxide 6 (formed by hydrolysis of the corresponding Herz salt 1e) was the species reacting with the malononitrile to give the by-products 3, 4 and 5 was eliminated by treating a pure sample of oxide 6 with malononitrile and Hüg’s base. TLC analysis was unable to locate any of the above products.

Benzothiazoles have been prepared from Herz salts previously; however, the procedure involved reduction of the heterocyclic dithiazole ring to afford the aminobenzenethiol, which is then cyclised to the benzothiazole.$^1$ Since under our reaction conditions such a reduction and cyclisation are not feasible an alternative pathway must be operating.

We postulate (Scheme 2) that malononitrile attacks the dithiazolium nitrogen $^1$ to afford the adduct 7 which ring opens to the imine 8. Cyclisation by the highly nucleophilic sulfur followed by proton transfer could yield benzothiazole 9 which

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Table 1  Ylidenes 2 derived from Herz salts 1 by treatment with malononitrile in the presence of Hüg’s base

<table>
<thead>
<tr>
<th>Ylidene</th>
<th>R$^1$</th>
<th>R$^2$</th>
<th>R$^3$</th>
<th>UV–vis $\lambda_{max}$/nm (log $\varepsilon$)</th>
<th>$^{13}$C (ppm) C(CN)$_2$</th>
<th>Yield (%)</th>
</tr>
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<tbody>
<tr>
<td>2a</td>
<td>H</td>
<td>H</td>
<td>H</td>
<td>575 (4.35)</td>
<td>61.2</td>
<td>11</td>
</tr>
<tr>
<td>2b</td>
<td>Me</td>
<td>H</td>
<td>H</td>
<td>569 (4.37)</td>
<td>60.8</td>
<td>16</td>
</tr>
<tr>
<td>2c</td>
<td>H</td>
<td>Me</td>
<td>H</td>
<td>Nd$^3$</td>
<td>61.5</td>
<td>5$^a$</td>
</tr>
<tr>
<td>2d</td>
<td>H</td>
<td>H</td>
<td>Me</td>
<td>N.d.$^3$</td>
<td>62.8</td>
<td>5$^a$</td>
</tr>
<tr>
<td>2e</td>
<td>MeO</td>
<td>H</td>
<td>H</td>
<td>564 (4.33)</td>
<td>60.2</td>
<td>11</td>
</tr>
<tr>
<td>2f</td>
<td>H</td>
<td>MeO</td>
<td>H</td>
<td>554 (4.41)</td>
<td>59.7</td>
<td>14</td>
</tr>
<tr>
<td>2g</td>
<td>Me</td>
<td>Me</td>
<td>H</td>
<td>569 (4.34)</td>
<td>61.3</td>
<td>13</td>
</tr>
<tr>
<td>2h</td>
<td>Me</td>
<td>H</td>
<td>Me</td>
<td>569 (4.34)</td>
<td>62.2</td>
<td>15</td>
</tr>
<tr>
<td>2i</td>
<td>–CH–CH–CH–</td>
<td>H</td>
<td>530 (4.41)</td>
<td>61.3</td>
<td>40</td>
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</tr>
<tr>
<td>2j</td>
<td>=N–S–N=</td>
<td>H</td>
<td>517 (4.35)</td>
<td>63.3</td>
<td>30</td>
<td></td>
</tr>
</tbody>
</table>

$^a$ The 5- and 7-methyl derivatives 2c and 2d were obtained as an inseparable mixture from 3-methylanthline. $^b$ N.d. = not determined.
could lose sulfur via a chain extension mechanism to give 4. Alternatively loss of HCN from 9 could occur first to give 10 followed by loss of sulfur to afford benzothiazole 3. It is also possible that cyanide could play a part in the desulfurisation of 9 and 10 thus generating the thiocyanate anions which could displace the activated chlorine atoms, particularly in the starting Herz salt 1. This could presumably lead to the subsequent formation of benzothiazole 5.

In conclusion we have demonstrated that the condensation of malononitrile with Herz salts in the presence of base gives highly coloured ylidemalononitriles in low to modest yields in somewhat complex reactions which can include direct attack of the heterocyclic ring by malononitrile to give various benzothiazole by-products.

**Experimental**

All reactions and column eluents were monitored by TLC using commercial aluminum backed thin-layer chromatography (TLC) plates (Merck Kieselgel 60 F254). The plates were observed under UV light at 254 and 366 nm. The technique of dry flash chromatography was used throughout for all non-TLC scale chromatographic separations using Sorbsil C60 M40 silica. Petrol refers to light petroleum, bp 60-80 °C.

Melting points were determined using a Reichert Koffer hot-stage apparatus. Solvents used for recrystallisation are indicated after the melting point. UV spectra were obtained using a Perkin-Elmer Lambda II spectrometer and inflections are identified by the abbreviation ‘inf’. IR spectra were recorded on a Perkin-Elmer 1710 FT spectrometer and strong, medium and weak peaks are represented by s, m and w respectively. 1H NMR spectra were recorded on Bruker RX-400 (400 MHz) and Bruker AM500 (500 MHz) machines. A doublet of sextets is represented by dhe. Deuterated solvents were used for homonuclear lock and the signals are referenced to the deuterated solvent peaks. Mass spectra were recorded on a VG micromass 7070E or a VG Autospec “Q” mass spectrometer. Microanalyses were performed on a Perkin-Elmer 2400 CHN Analyser.

**Reaction of Herz salts with malononitrile**

**Typical procedure.** To a stirred suspension of 6-chloro-1,2,3-benzodithiazol-2-ium chloride 1a10 (223 mg, 1 mmol) in DCM (25 ml) at ca. 20 °C, malononitrile (66 mg, 1 mmol) was added followed by the addition of Hüning’s base (348 µl, 2 mmol). After 1 h TLC indicated a deep blue product and chromatography (DCM) gave (6H-1,2,3-benzodithiazol-6-ylidene)-propanedinitrile 2a (24 mg, 11%) as deep blue prisms, mp 283–285 °C (from glacial acetic acid) (Found: C, 49.7; H, 1.5; N, 19.1. C11H8N2S2 requires C, 49.8; H, 1.4; N, 19.35; \( \lambda_{\text{max}}(\text{DCM})/\text{nm} \) 228 (log ε 3.66), 276 inf (3.96), 281 (3.99), 333 inf (4.00), 343 (4.12), 395 (3.23), 551 inf (4.33), 575 (4.35), 619 inf (4.13); \( \nu_{\text{max}}(\text{Nujol})/\text{cm}^{-1} \) 3096w, 3068w and 3047w (Ar CH), 2205s (CN), 2175s (CN), 1596s (C=N), 1513s (C=C), 1489s, 1455s, 1407s, 1355m, 1339m, 1245m, 1199w, 117w, 1150m, 1029m, 985m, 902m, 870m, 799s, 725m, 649m; \( \delta_{\text{H}}(400 \text{ MHz}; \text{DMSO-DCl}) \) 7.88 (1H, d, \( J = 9.6 \text{ Hz} \), Ar H-4), 7.82 (1H, d, \( J = 2.0 \text{ Hz} \), Ar H-7), 7.50 (1H, dd, \( J = 2.0, 9.6 \text{ Hz} \), Ar H-5); \( \delta_{\text{C}}(100 \text{ MHz}; \text{DMSO-DCl}) \) 159.0, 153.2, 152.0, 129.0 (Ar CH), 128.2 (Ar CH), 116.4 (CN), 116.4 (CN), 109.8 (Ar CH), 61.2 (C(CN)), \( m/z \) (EI) 217 (M+, 100%), 190 (M+ – CHN, 5), 173 (4), 160 (28), 155 (4), 141 (9), 127 (5), 114 (5), 87 (3), 76 (C2H4), 74, 64 (S2, 9) (Found: M+, 216.9749, C11H8N2S2 requires M+, 216.9768).

**[(4-Methyl-6H-1,2,3-benzodithiazol-6-ylidene)propanedinitrile](#)**

Similar treatment of 6-chloro-4-methyl-1,2,3-benzodithiazol-2-ium chloride 1b10 with malononitrile and Hüning’s base gave the title compound 2b (16%) as lustrous green–brown solid, mp > 300 °C (from glacial acetic acid) (Found: C, 51.8; H, 2.2; N, 18.0. C11H9N2S2 requires C, 51.95; H, 2.2; N, 18.2%; \( \lambda_{\text{max}}(\text{DCM})/\text{nm} \) 228 (log ε 3.87), 275 inf (3.99), 279 (4.01), 347 (4.14), 395 (3.44), 414 (3.42), 545 inf (4.35), 569 (4.37), 610 inf (4.16); \( \nu_{\text{max}}(\text{Nujol})/\text{cm}^{-1} \) 3068w (Ar CH), 2201s (CN), 1603s (C=N), 1507s (C=C), 1432m, 1399m, 1319s, 1253w, 1133m, 1037w, 985m, 904m, 881w, 860w, 840w, 826w, 809m, 736m, 577w; \( \delta_{\text{H}}(400 \text{ MHz}; \text{DMSO-DCl}) \) 7.70 (1H, d, \( J = 2.0 \text{ Hz} \), Ar H), 7.31 (1H, m, Ar H), 2.53 (3H, d, \( J = 1.1 \text{ Hz} \), CH3); \( \delta_{\text{C}}(100 \text{ MHz}; \text{DMSO-DCl}) \) 159.8, 153.2, 152.6, 138.4, 126.5 (Ar CH), 116.5 (C=N), 116.5 (CN), 108.7 (Ar CH), 60.8 [C(CN)]; \( m/z \) (EI) 231 (M+, 100%), 190 (M+ – CHN, 5), 173 (4), 162 (12), 155 (4), 141 (9), 127 (5), 114 (5), 87 (3), 76 (C2H4), 74, 64 (S2, 9) (Found: M+, 216.9749, C11H9N2S2 requires M+, 216.9768).

**[(5-Methyl-6H-1,2,3-benzodithiazol-6-ylidene)propanedinitrile](#)**

Similar treatment of a mixture of 6-chloro-5-methyl-1,2,3-benzodithiazol-2-ium chloride 1c12 and 6-chloro-7-methyl-1,2,3-benzodithiazol-2-ium chloride 1d with malononitrile and Hüning’s base gave a mixture of the title compounds 2c and 2d (5%) as blue needles, mp > 300 °C (from glacial acetic acid) (Found: C, 52.05; H, 2.0; N, 18.0. C11H8N2S2 requires C, 51.95; H, 2.2; N, 18.2%; \( \delta_{\text{H}}(400 \text{ MHz}; \text{DMSO-DCl}) \) 7.82 (1H, s, Ar H, J = 2.0 Hz, Ar H-7), 7.50 (1H, d, \( J = 9.6 \text{ Hz} \), Ar H-5); \( \delta_{\text{C}}(100 \text{ MHz}; \text{DMSO-DCl}) \) 159.8, 153.2, 152.6, 138.4, 126.5 (Ar CH), 116.5 (C=N), 116.5 (CN), 108.7 (Ar CH), 60.8 [C(CN)]; \( m/z \) (EI) 231 (M+, 100%), 203 (2), 198 (3), 171 (3), 140 (4), 128 (3), 115 (3), 101 (2), 89 (2), 64 (4) (Found: M+, 230.9912, C11H8N2S2 requires M+, 230.9925).
(4-Methoxy-6H-1,2,3-benzodithiazol-6-yldiene)propanedinitrile 2e

Similar treatment of 6-chloro-4-methoxy-1,2,3-benzodithiazol-2-ium chloride 1e with malononitrile and Hünig's base gave the title compound 2e (11%) as lustrous green needles, mp > 300 °C (from glacial acetic acid) (Found: C, 48.3; H, 2.0; N, 16.7. C_{10}H_{13}N_{2}O requires C, 48.6; H, 2.0; N, 17.0%). \( \lambda_{\text{max}} \) (DCM)/nm 308 (log ε 2.24), 324 (2.57), 340 (2.87), 352 (2.94), 380 (3.18), 400 (3.35), 410 (3.43), 420 (3.55), 430 (3.66), 450 (3.78), 460 (3.87), 470 (3.94), 480 (3.95), 490 (3.98), 500 (4.01), 510 (4.03), 520 (4.05), 530 (4.07), 540 (4.09). mp 285–286 °C (from glacial acetic acid), identical with an authentic sample.

(5-Methoxy-6H-1,2,3-benzodithiazol-6-yldiene)propanedinitrile 2f

Similar treatment of 6-chloro-5-methoxy-1,2,3-benzodithiazol-2-ium chloride 1f with malononitrile and Hünig's base gave the title compound 2f (14%) as green–brown needles, mp > 300 °C (from glacial acetic acid) (Found: C, 48.3; H, 1.9; N, 16.7. C_{10}H_{12}N_{2}O requires C, 48.6; H, 2.0; N, 17.0%). \( \lambda_{\text{max}} \) (DCM)/nm 288 (log ε 2.87), 305 (2.96), 317 (2.99), 320 (3.00), 335 (3.06), 345 (3.14), 355 (3.20), 360 (3.25), 370 (3.30), 380 (3.35), 390 (3.40), 400 (3.45), 410 (3.50), 420 (3.55), 430 (3.60), 440 (3.65), 450 (3.70), 460 (3.75), 470 (3.80), 480 (3.85), 490 (3.90), 500 (3.95), 510 (4.00), 520 (4.05), 530 (4.10), 540 (4.15). mp 285–286 °C (from glacial acetic acid), identical with an authentic sample.

(4,7-Dimethyl-6H-1,2,3-benzodithiazol-6-yldiene)propanedinitrile 2h

Similar treatment of 6-chloro-4,7-dimethyl-1,2,3-benzodithiazol-2-ium chloride 1h with malononitrile and Hünig's base gave the title compound 2h (15%) as lustrous green needles, mp > 270 °C (from glacial acetic acid) (Found: C, 53.9; H, 2.7; N, 17.1. C_{10}H_{14}N_{2}S requires C, 53.9; H, 2.9; N, 17.1%). \( \lambda_{\text{max}} \) (DCM)/nm 229 (log ε 3.86), 276 (3.88), 318 (3.59), 353 (4.19), 408 (3.54), 427 (3.50), 545 (4.37), 569 (4.34), 606 (4.42), 291 (Nujol)/cm \(^{-1}\) 2199 (CN), 1670s (C–N), 1511s (C=C), 1493s, 1425s, 1405s, 1392s, 1355m, 1290m, 1241m, 1156w, 1122w, 1059m, 1033m, 962m, 909m, 896m, 880m, 834m, 741w, 722w, 685s, 654m, 640 (400 MHz; DMSO-d\(_6\)) 7.36 (1H, d, J 1.2 Hz, Ar H-5), 2.57 (3H, s, CH\(_3\)), 2.49 (3H, hidden by DMSO-d\(_6\)); CH\(_3\)) 100MHz (DCM) 3H, 140.0, 139.4, 138.9, 129.8, 128.6, 128.4, 127.7 (d, 7J 2.6 Hz, Ar H-7), 2.52 (3H, s, CH\(_3\)), 2.48 (3H, s, CH\(_3\)); \( \delta_{\text{H}} \) (DMSO-d\(_6\)) 159.6, 152.5, 150.3, 153.2, 152.4, 116.6 (C), 116.5 (C), 106.0 (Ar CH), 102.5 (Ar CH), 60.2 (C[Nj]), 56.8 (CH\(_2\)O); m/z (EI) 247 (M\(^{+}\), 100%), 232 (M\(^{-}\) – CH\(_3\)O, 13), 215 (M\(^{-}\) – CH\(_3\)N, 15), 214 (M\(^{-}\) – CH\(_3\)N, 10), 119 (M\(^{-}\) – N, 94), 64 (S\(_2\)H, 8) (Found: M\(^{+}\), 246.9879. C\(_8\)H\(_6\)N\(_2\)S\(_2\) requires M, 246.9874).
methoxy-2,3-dihydrobenzothiazole-2,2-dicarbonitrile

Further elution (petrol–DCM. 1 : 3) gave 4-methoxy-6-thiocyanatobenzothiazole-2-carbonitrile 5 (24 mg, 5%) cream coloured needles, mp 169–172 °C (from cyclohexane–pentane) (Found: C, 48.3; H, 2.0; N, 16.9. C<sub>16</sub>H<sub>14</sub>N<sub>2</sub>O<sub>2</sub> requires C, 48.6; H, 2.0; N, 17.0%); δ<sub>max</sub>(DCM)/nm 303 (log ε 4.06), 344 (3.84); δ<sub>max</sub>(Nujol)/cm<sup>-1</sup> 3082w and 3062w (Ar CH), 1346; δ<sub>max</sub> (Nujol)/cm<sup>-1</sup> 1556, 1437, 1387, 1277, 1146 (Ar CH), 1129 (CN), 1097 (SCN), 1092 (Ar CH), 573 (CH<sub>2</sub>O); m/z (EI) 247 (M<sup>+</sup>, 62%), 220 (M<sup>+</sup> – CHN, 13), 218 (M<sup>+</sup> – CH<sub>2</sub>N, 100), 204 (4), 191 (8), 159 (18), 149 (6), 107 (3), 94 (6), 69 (14) (Found: M<sup>+</sup> 246,9908. C<sub>16</sub>H<sub>14</sub>N<sub>2</sub>O<sub>2</sub> requires M, 246,9874); LSMS: (EI, B/E of m/z 247) 232 (2%), 218 (100), 204 (2), 191 (13), 159 (7); (EI, B/E of m/z 218) 247 (M<sup>+</sup>, 100%). Further elution (DCM) gave {4-methoxy-6H-1,2,3-benzodithiazol-6-ylidene)propanedinitrile 2e (54 mg, 11%) as green needles, mp > 300 °C (from glacial acetic acid), identical to that described above. A final elution (DCM) gave 6-chloro-4-methoxy-2,3-dihydrobenzothiazole-2,2-dicarbonitrile 4 (6 mg, 1%) as faint yellow needles, m/z (EI) 251 (M<sup>+</sup>, 3%), 224 (M<sup>+</sup> – HCN, 49), 195 (M<sup>+</sup> – HCN, –CHO, 100), 189 (M<sup>+</sup> – HCN, –Cl, 6), 181 (15), 159 (26), 129 (9), 93 (12), 85 (30), 79 (13), 71 (52), 62 (7).}

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