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# Rearrangements of the [2+2]-cycloadducts of DDQ and 2-ethynylpyrroles

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ABSTRACT

The [2+2]-cycloadducts of DDQ and 2-ethynylpyrroles, upon ethanolysis (reflux, 15 min or room temperature, 24 h), rearrange from bicyclo[4.2.0]octadienediones to bicyclo[3.2.0]heptadienone- and cyclobutenyl-dihydrofuranone moieties in 55–83% yields, the former rearrangement being the major direction. Benzoquinone ring cleavage is regioselective to afford mostly bicyclo[3.2.0]heptadienone-pyrrole ensembles (85–90% selectivity) in 39–78% yields. The only exception is when the starting compounds contain an ethoxycarbonyl substituent and the pyrrole counterpart is a 4,5,6,7-tetrahydroindole fragment. In this case, the ratio of the rearrangement products is 1:1.2 in a total yield of 83%. An important feature of the dihydrofuranone pathway rearrangement is its 100% diastereoselectivity.



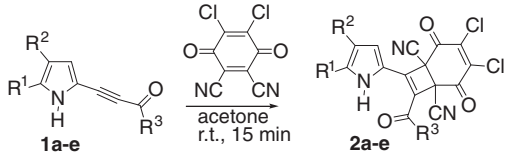
Recently, we revealed[1] an extremely facile [2+2]-cycloaddition of 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) to the readily available[2] 2-ethynylpyrroles **1a–e**, bearing acyl- or alkoxycarbonyl groups at the triple bond, which makes the cycloadducts **2a–e** easily accessible for further investigations (Scheme 1).

Herein, we report on the skeletal rearrangements of cycloadducts **2a–e** which occur in ethanol (reflux or room temperature) to afford pyrrolylbicyclo[3.2.0]heptadienones **3a–e** and pyrrolylcyclobutenyl-dihydrofuranones **4a–e** (ratio 44:56–90:10, depending on the structure of the starting compound **2a–e**), in total yields ranging from 55% to 83% (Scheme 2, Table 1).[3]

As follows from Table 1, the reaction was regioselective proceeding with preferable formation of bicycloheptadienones **3a–d** (selectivity 85–90%), while dihydrofuranones **4a–d** were the minor products (the latter products were identified by $^1$H NMR). The only exception was cycloadduct **2e**, which gave products **3e** and **4e** in a ratio of 44:56 (isolated yields, 39% and 44%).

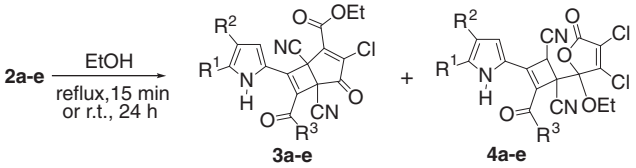
The structures of the rearrangement products were proved unambiguously by X-ray crystallographic analysis as seen in the example of diethyl 3-chloro-1,5-dicyano-4-oxo-7-(4,5,6,7-tetrahydro-1*H*-indol-2-yl)bicyclo[3.2.0]hepta-2,6-diene-2,6-dicarboxylate (**3e**) (Fig. 1) and ethyl 3,4-dicyano-4-(3,4-dichloro-2-ethoxy-5-oxo-2,5-dihydro-2-furanyl)-2-(4,5,6,7-tetrahydro-1*H*-indol-2-yl)-1-cyclobutene-1-carboxylate (**4e**) (Fig. 2).[4]

Also, the $^1$H and $^{13}$C NMR spectra entirely supported the structures of rearrangement products **3a–e** and **4e**. The signals of the




| Cycloadduct | $R^1$ | $R^2$ | $R^3$ |
|---|---|---|---|
| **2a** | Ph | H | Ph |
| **2b** | 4-$ClC_6H_4$ | H | Ph |
| **2c** | 4-$MeOC_6H_4$ | H | 4-$O_2NC_6H_4$ |
| **2d** | $(CH_2)_4$ | | Ph |
| **2e** | $(CH_2)_4$ | | OEt |

**Scheme 1.**




**Scheme 2.**

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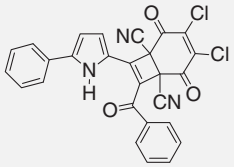
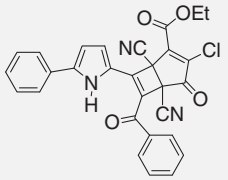
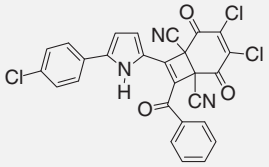
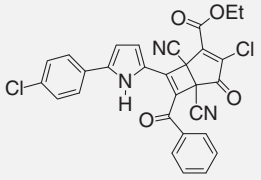
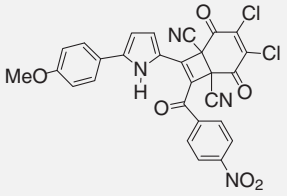
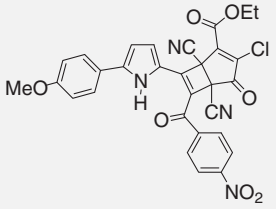
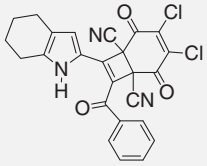
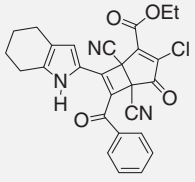
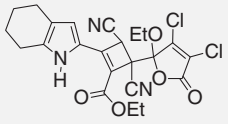
**Table 1**
Rearrangement products **3a–e** and **4e** were synthesized according to Scheme 2

| Entry | Cycloadduct | Rearrangement product | Yield (%) |
|---|---|---|---|
| 1 |  **2a** |  **3a** | 55 |
| 2 |  **2b** |  **3b** | 57 |
| 3 |  **2c** |  **3c** | 78 |
| 4 |  **2d** |  **3d** | 71 |
| 5 | |  **3e**  **4e** | 39<br>44 |

quaternary carbon atoms C1 and C5 in the cyclobutene ring (53.1–48.1 ppm) and those of the three carbonyl carbons in the region 187.8–160.5 ppm were important for the structural assignment of the $^{13}$C NMR spectra of compounds **3a–e**. The signals at 162.2, 160.9, 50.6, and 34.6 ppm in the $^{13}$C spectrum of dihydrofuranone **4e** were attributable to two carbonyl carbon atoms and carbons C3 and C4 of cyclobutene ring bonded to the CN-groups, respectively. The carbon atom C2 in the dihydrofuranone ring of this compound resonated at 104.9 ppm. In the $^{1}$H NMR spectrum of compound **4e**, the proton of the cyclobutene ring appeared at 4.36 ppm and displayed long range correlations (2D HMBC) with the carbon atoms at 50.6, 104.9, 106.0, 114.0 (CN), and 144.8 (C2 of pyrrole ring). The NOEs between this proton and H3 of the pyrrole ring (6.60 ppm) and the protons of the $OCH_2$ group (3.86 ppm) were observed in the 2D NOESY spectrum.

The rearrangement of bicyclo[4.2.0]octadienediones **2a–e** into bicyclo[3.2.0]heptadienones **3a–e** is likely triggered by the addition of ethanol to the quinone carbonyl group (at C2). The intermediate hemiacetal **A** then undergoes ring opening to form the ester group with simultaneous cleavage of the C1–C2 bond. This leads to the formation of the carbanion center at the C1 which attacks the C3 carbon atom in an intramolecular nucleophilic substitution

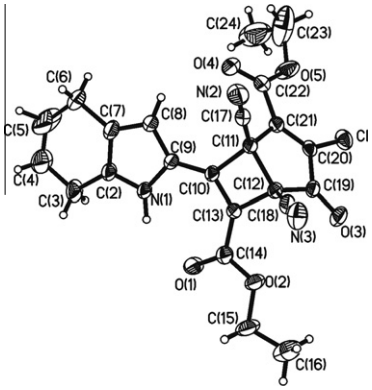



**Figure 1.** X-ray crystal structure of **3e**.

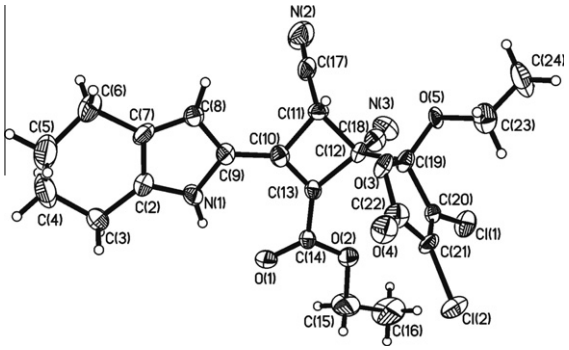
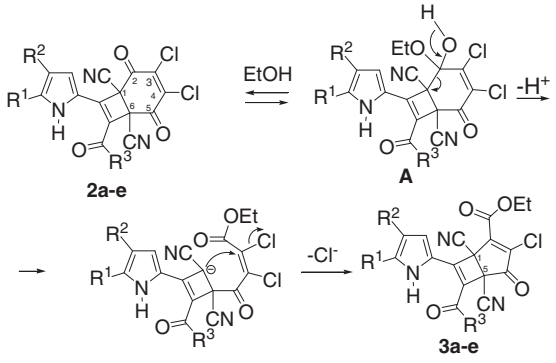



**Figure 2.** X-ray crystal structure of **4e**.

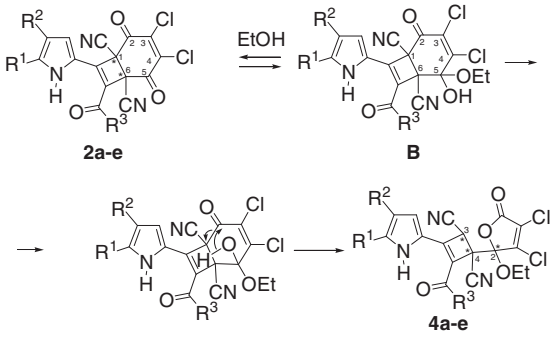



**Scheme 3.**

with elimination of hydrogen chloride. Finally, the ring contraction occurs to yield the products **3a–e** (Scheme 3).

The formation of furanones **4a–e** occurs by similar addition of ethanol to the other quinone carbonyl (at C5). In the intermediate hemiacetal **B**, the hydroxy group attacks the C2 carbonyl group with ring opening via cleavage of the same C1–C2 bond. This is accompanied by a concerted proton transfer to the carbanion-like C1 center (Scheme 4).

As compared to the starting cycloadduct **2e**, in furanone **4e**, the configuration of the C3 atom in the cyclobutene ring may change. Moreover, another asymmetric center is present at the C2 atom in the dihydrofuranone ring. Therefore, two diastereomeric pairs of **4e** may exist. However, in the $^{1}$H and $^{13}$C NMR spectra, the signals of only one diastereomer were detected (no signal doublings are discernible). The relative configuration of this diastereomer shown in Figure 2 suggests that the cleavage of the C1–C2 bond in compound **2e** and formation of the C3–H bond occur from the same side of the four-membered ring.




**Scheme 4.**

Similar bicyclo[4.2.0]octadienediones, prepared by photoaddition of diphenylacetylene to benzo- and naphthoquinones, upon alcoholysis, rearranged via the cleavage of the cyclobutene ring.[5] This differs completely from the rearrangement we observed here.

The rearrangement products **3a–e** and **4a–e** are interesting compounds due to the combination of densely functionalized cyclobutene and pyrrole scaffolds. Only a few representatives containing exhaustively substituted cyclobutene rings are known[6,7] and their syntheses are multistep and laborious.[8] In addition, some are employed as key intermediates in Corey's brefeldin A synthesis.[9]

The rearrangements observed herein enable easy entry to hitherto unknown densely functionalized heterocyclic ensembles with rare combinations of heterocycles and functional groups.

## Acknowledgments

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## References and notes

1. Trofimov, B. A.; Sobenina, L. N.; Stepanova, Z. V.; Ushakov, I. A.; Sinegovskaya, L. M.; Vakul'skaya, T. I.; Mikhaleva, A. I. *Synthesis* **2010**, 470–477.
2. (a) Trofimov, B. A.; Stepanova, Z. V.; Sobenina, L. N.; Mikhaleva, A. I.; Ushakov, I. A. *Tetrahedron Lett.* **2004**, *45*, 6513–6516; (b) Trofimov, B. A.; Sobenina, L. N.; Stepanova, Z. V.; Petrova, O. V.; Ushakov, I. A.; Mikhaleva, A. I. *Tetrahedron Lett.* **2008**, *49*, 3946–3949.
3. Typical procedure. Rearrangement of cycloadducts **2a–d**. Cycloadduct **2a–d** (0.1 g) was refluxed for 15 min in EtOH (20 mL). Bright red crystals begin to precipitate from the hot solution after 5–10 min. After cooling to room temperature the crystals were filtered and dried to give bicyclo[3.2.0] heptadienones **3a–c**. The red crystals of compound **3d** were filtered from the solution after 24 h. In the case of cycloadduct **2e**, formed after 24 h the mixture of yellow and red crystals was filtered and fractionated by silica gel column chromatography ($CH_2Cl_2$) to afford compounds **3e** and **4e**. All new compounds exhibited spectral data consistent with their structures. Selected spectral data: *Ethyl 7-benzoyl-3-chloro-6-[5-phenyl-1H-pyrrol-2-yl]-1,5-dicyano-4-oxobicyclo [3.2.0]hepta-2,6-diene-2-carboxylate* (**3a**). Red crystals; mp: 234–236 °C; IR (KBr, $cm^{-1}$) 3441 (NH), 2250 (CN), 1749, 1717 (C=O), 1627 (C=C); $^{1}$H NMR (400.13 MHz, $CDCl_3$) $\delta$ 12.98 (br s, 1H, NH), 8.06 (m, 2H, CH-2,6 COPh), 7.76 (m, 2H, CH-2,6 Ph), 7.65 (m, 1H, CH-4 COPh), 7.58 (m, 2H, CH-3,5 COPh), 7.50 (m, 3H, H-3, CH-3,5 Ph), 7.42 (m, 1H, CH-4 Ph), 6.90 (dd, $^{3}J$ = 4.4 Hz, $^{4}J$ = 2.5 Hz, 1H, H-4), 4.51 (q, $J$ = 7.2 Hz, 2H, $OCH_2$), 1.44 (t, $J$ = 7.2 Hz, 3H, $CH_3$); $^{13}$C NMR (100.6 MHz, $CDCl_3$) $\delta$ 187.8, 183.7, 160.5, 148.7, 144.7, 143.0, 141.8, 136.4, 133.6, 129.9, 129.6, 129.5, 129.0, 128.5, 125.6, 125.3, 123.8, 115.2, 113.0, 112.0, 111.9, 64.0, 53.2, 48.3, 14.1. Anal. Calcd. for $C_{29}H_{18}ClN_3O_4$: C, 68.58; H, 3.57; Cl, 6.98; N, 8.27. Found: C, 68.79; H, 3.46; Cl, 7.20; N, 8.68.
*Ethyl 7-benzoyl-3-chloro-6-[5-(4-chlorophenyl)-1H-pyrrol-2-yl]-1,5-dicyano-4-oxobicyclo[3.2.0]hepta-2,6-diene-2-carboxylate* (**3b**). Red crystals; mp: 233–234 °C; IR (KBr, $cm^{-1}$) 3436 (NH), 2254 (CN), 1749, 1716 (C=O), 1631 (C=C); $^{1}$H NMR (400.13 MHz, $CDCl_3$) $\delta$ 12.99 (br s, 1H, NH), 8.08 (m, 2H, CH-2,6 COPh), 7.68 (m, 2H, CH-2,6 Ph), 7.64 (m, 1H, CH-4 COPh), 7.58 (m, 2H, CH-3,5 COPh), 7.52 (dd, $^{3}J$ = 4.1 Hz, $^{4}J$ = 1.6 Hz, 1H, H-3), 7.46 (m, 2H, CH-3,5 Ph), 6.90 (dd, $^{3}J$ = 4.1 Hz,

$^4J$ = 2.4 Hz, 1H, H-4), 4.54 (q, $J$ = 7.0 Hz, 2H, $OCH_2$), 1.44 (t, $J$ = 7.0 Hz, 3H, Me); $^{13}C$ NMR (100.6 MHz, $CDCl_3$) $\delta$ 187.8, 183.7, 160.5, 148.8, 144.6, 141.9, 141.4, 136.2, 135.8, 133.7, 129.8, 129.1, 128.6, 128.1, 126.7, 125.5, 123.8, 115.7, 113.0, 112.0, 111.8, 64.0, 53.2, 48.3, 14.1. Anal. Calcd. for $C_{29}H_{17}Cl_2N_3O_4$: C, 64.22; H, 3.16; Cl, 13.07; N, 7.75. Found: C, 64.29; H, 3.30; Cl, 13.38; N, 7.58.

*Ethyl 7-(4-nitrobenzoyl-3-chloro-6-[5-(4-methoxyphenyl)-1H-pyrrol-2-yl]-1,5-dicyano-4-oxobicyclo[3.2.0]hepta-2,6-diene-2-carboxylate* (**3c**). Cherry red crystals; mp: 279–280 °C; IR (KBr, $cm^{-1}$) 3449 (NH), 2248 (CN), 1746, 1716 (C=O), 1626 (C=C); $^1H$ NMR (400.13 MHz, $CDCl_3$) $\delta$ 12.94 (br s, 1H, NH), 8.41 (m, 2H, CH-2,6 4-$NO_2C_6H_4$), 8.15 (m, 2H, CH-2,6 4-$MeOC_6H_4$), 7.74 (m, 2H, CH-3,4 4-$NO_2C_6H_4$), 7.63 (dd, $^3J$ = 4.1 Hz, $^4J$ = 1.6 Hz, 1H, H-3), 7.03 (m, 2H, CH-3,4 4-$MeOC_6H_4$), 6.91 (dd, $^3J$ = 4.1 Hz, $^4J$ = 2.4 Hz, 1H, H-4), 4.51 (q, $J$ = 7.1 Hz, 2H, $OCH_2$), 3.88 (s, 3H, MeO), 1.44 (t, $J$ = 7.1 Hz, 3H, Me); $^{13}C$ NMR (100.6 MHz, $CDCl_6$) $\delta$ 185.7, 183.7, 161.6, 159.9, 153.3, 149.9, 144.8, 142.4, 141.9, 129.1, 127.4, 123.8, 121.8, 121.5, 121.3, 120.5, 115.3, 115.1, 113.2, 112.8, 111.7, 63.9, 55.5, 53.4, 48.7, 14.2. Anal. Calcd. for $C_{30}H_{19}ClN_4O_7$: C, 61.81; H, 3.29; Cl, 6.08; N, 9.61. Found: C, 61.59; H, 3.30; Cl, 5.88; N, 9.48.

*Ethyl 6-benzoyl-3-chloro-1,5-dicyano-4-oxo-7-(4,5,6,7-tetrahydro-1H-indol-2-yl) bicyclo[3.2.0]-hepta-2,6-diene-2-carboxylate* (**3d**). Red crystals; mp: 233–235 °C; IR (KBr, $cm^{-1}$): 3459 (NH), 2243 (CN), 1743, 1719 (C=O), 1628 (C=C); $^1H$ NMR (400.13 MHz, $CDCl_3$) $\delta$ 12.17 (br s, 1H, NH), 8.04 (m, 2H, CH-2,6 Ph), 7.64 (m, 1H, CH-4 Ph), 7.58 (m, 2H, CH-3,5 Ph), 7.20 (d, $^3J$ = 1.9 Hz, 1H, H-3), 4.53 (q, 2H, $J$ = 7.2 Hz, $OCH_2$), 2.81 (m, 2H, $CH_2$-7), 2.65 (m, 2H, $CH_2$-4), 1.90 (m, 2H, $CH_2$-5), 1.83 (m, 2H, $CH_2$-6), 1.48 (t, 3H, $J$ = 7.2 Hz, $CH_3$); $^{13}C$ NMR (100.6 MHz, $CDCl_3$) $\delta$ 187.3, 183.8, 160.5, 148.2, 144.7, 143.4, 141.7, 136.6, 133.2, 128.9, 128.3, 126.5, 123.6, 120.7, 112.5, 112.3, 112.2, 63.8, 53.1, 48.2, 24.1, 23.1, 23.0, 22.4, 14.0. Anal. Calcd. for $C_{27}H_{20}ClN_3O_4$: C, 66.74; H, 4.15; Cl, 7.30; N, 8.65. Found: C, 66.63; H, 4.50; Cl, 7.59; N, 8.79.

*Diethyl 3-chloro-1,5-dicyano-4-oxo-7-(4,5,6,7-tetrahydro-1H-indol-2-yl)bicyclo [3.2.0]-hepta-2,6-diene-2,6-dicarboxylate* (**3e**). Red crystals, mp 230–231 °C. IR (KBr, $cm^{-1}$): 3300 (NH), 2248 (CN), 1755, 1716, 1685 (CO), 1615 (C=C); $^1H$ NMR (400.13 MHz, $CDCl_3$) $\delta$ 10.87 (br s, 1H, NH), 7.00 (d, $^3J$ = 1.9 Hz, 1H, H-3), 4.48 (q, 2H, $J$ = 7.1 Hz, $CH_2OC(O)C$-6), 4.32 (m, 2H, $CH_2OC(O)C$-2), 2.68 (m, 2H, $CH_2$-7), 2.55 (m, 2H, $CH_2$-4), 1.82 (m, 2H, $CH_2$-5), 1.75 (m, 2H, $CH_2$-6), 1.43 (t, $J$ = 7.1 Hz, 3H, $CH_3$), 1.38 (t, $J$ = 7.1 Hz, 3H, $CH_3$); $^{13}C$ NMR (100.6 MHz, $CDCl_3$) $\delta$ 182.9, 162.8, 160.5, 148.2, 144.2, 142.0, 141.8, 123.9, 121.5, 119.2, 111.9, 111.2, 105.7, 63.8, 62.2, 52.0, 47.4, 23.8, 23.2, 22.8, 22.6, 14.2, 14.0. Anal. Calcd. for $C_{23}H_{20}ClN_3O_5$: C, 60.86; H, 4.44; Cl, 7.81; N, 9.26. Found: C, 60.53; H, 4.55; Cl, 8.00; N, 9.12.

*Ethyl 3,4-dicyano-4-(3,4-dichloro-2-ethoxy-5-oxo-2,5-dihydro-2-furanyl)-2-(4,5,6,7-tetrahydro-1H-indol-2-yl)-1-cyclobutene-1-carboxylate* (**4e**). Yellow crystals; mp: 211–212 °C; IR (KBr, $cm^{-1}$): 3285 (NH), 2248 (CN), 1807 (CO), 1686 (CO(O)), 1619 (C=C). $^1H$ NMR (400.13 MHz, $CDCl_3$) $\delta$ 10.71 (br s, 1H, NH), 6.60 (d, $J$ = 2.0 Hz, 1H, H-3), 4.36 (s, 1H, CH-CN), 4.31 (m, 1H, $CH_2C$=O), 4.21 (m, 1H, $CH_2C$=O), 3.58 (m, 2H, $OCH_2$), 2.66 (m, 2H, $CH_2$-7), 2.53 (m, 2H, $CH_2$-4), 1.82 (m, 2H, $CH_2$-5), 1.75 (m, 2H, CH2-6), 1.35 (t, $J$ = 7.1 Hz, 3H, $CH_3$), 1.33 (t, $J$ = 7.1 Hz, 3H, $CH_3$); $^{13}C$ NMR (100.6 MHz, $CDCl_3$) $\delta$ 162.2, 160.9, 148.5, 144.8, 140.2, 125.0, 123.2, 121.9, 117.4, 114.2, 114.0, 106.0, 104.9, 62.0, 61.9, 50.6, 34.6, 23.6, 23.2, 22.7, 22.6, 14.8, 14.4. Anal. Calcd. for $C_{23}H_{21}Cl_2N_3O_5$: C, 56.34; H, 4.32; Cl, 14.46; N, 8.57. Found: C, 56.74; H, 4.34; Cl, 14.53; N, 8.35.

4. The X-Ray diffraction study of **3e** was carried out using a Bruker SMART APEX2 CCD diffractometer at room temperature (Mo Kα radiation). X-Ray diffraction of **4e** was carried out with an Enraf-Nonius CAD-4 diffractometer at room temperature ($\omega/2\theta$-scanning, Mo Kα radiation, graphite monochromator). Crystalline structures of **3e** and **4a** were solved by direct methods followed by Fourier synthesis using SHELXS-97.[10] All non-hydrogen atoms were refined using anisotropic full-matrix approximation using SHELXL-97.[10] The coordinates of the hydrogen atoms were calculated. Atom coordinates, bond lengths, and angle values were deposited at Cambridge Crystallographic Data Centra (CCDC). These data are available via www.ccdc.cam.uk/conts/retrieving.html (or from CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44(0)1223 336 033; or deposit@ccdc.cam.ac.uk). Any request to the CCDC for data should quote the full literature citation and CCDC reference numbers 776907 and 776908 for **3e** and **4e**, respectively.

Crystal and experimental data for **3e**: $C_{23}H_{20}ClN_3O_5$, $M$ = 453.87, triclinic, $P\bar{1}$, $a$ = 8.211(1) Å, $b$ = 11.909(1) Å, $c$ = 12.942(1) Å, $\alpha$ = 108.80(2)°, $\beta$ = 96.10(2)°, $\gamma$ = 106.17(2)°, $V$ = 1123.5(2) Å$^3$, $Z$ = 2, $D_{calcd}$ = 1.34 g cm$^{-3}$, $\mu$ = 0.209 mm$^{-1}$, reflections observed/independent 8229/4225, 290 parameters refined, $R$ = 0.060 for 1731 reflections with [$F_0 > 4\sigma(F_0)$].

Crystal and experimental data for **4e**: $C_{23}H_{21}Cl_2N_3O_5$, $M$ = 490.33, monoclinic, $P2_1$, $a$ = 8.213(2) Å, $b$ = 7.710(2) Å, $c$ = 18.425(5) Å, $\beta$ = 91.22(3)°, $V$ = 1166.4(5) Å$^3$, $Z$ = 2, $D_{calcd}$ = 1.40 g cm$^{-3}$, $\mu$ = 0.318 mm$^{-1}$, reflections observed/independent 2353/2184, 300 parameters refined, $R$ = 0.079 for 1181 reflections with [$F_0 > 4\sigma(F_0)$].

Crystals of bicyclo[3.2.0]heptadienone **3e** form with one crystallographically independent molecule $C_{23}H_{20}ClN_3O_5$ (Fig. 1) taking a general position. The dihedral angle between the planes of the cyclobutene and cyclopentene rings is 115.6°. The cyclobutene fragment is almost planar, maximum atom deviation from the average plane does not exceed 0.02 Å. The C–C bond length in the cyclobutene ring is 1.58(8) Å. The dihedral angles formed by the cyclobutene and cyano substituents are 126.8° and 109.0°, respectively. The angle between the cyclobutene moiety and the average plane of the ester unit is 174.5°. The pyrrole fragment has an almost planar structure, maximum atom deviation from the plane being 0.005 Å. The dihedral angle between the cyclobutene and pyrrole planes is 170.8°.

The crystal structure of dihydrofuranone **4e** forms with one crystallographically independent molecule $C_{23}H_{21}Cl_2N_3O_5$ (Fig. 2), taking a general position. The cyclobutene fragment is almost planar, maximum atom deviation from the averaged plane did not exceed 0.002 Å. In the fragment, one of a longest ordinary C–C bond 1.62(1) Å was detected. The dihedral angles formed by the cyclobutene plane and cyano substituents are 53.4° and 71.1°, respectively. The angle between the cyclobutene moiety and the average plane of the ester unit is 172.0°. The pyrrole fragment has an almost planar structure, the maximum deviation of atoms from its plane being 0.01 Å. The dihedral angle between the cyclobutene and pyrrole planes equals 173.4°. The dihydrofuranone substituent is also almost planar, the maximum deviation of atoms from its plane being 0.01 Å. The dihedral angle formed by this fragment with the cyclobutene plane is 63.1°. The angle between the ethoxy group and the furan fragment is 82.5°.

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