Novel rearrangement in the reaction of 5-methyl-5H-iso-indolo [2,1-a]benzimidazole with maleimide derivatives. Stereochemical and X-ray structural study

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Abstract
In the reaction of 5-methyl-5H-isoindolo[2,1-a]benzimidazole 2 with N-arylmaleimides 3a–f a novel unexpected rearrangement led to the 3-(E)-1-(2,5-dioxo-1-R-tetrahydro-1H-3-pyrrolyl)-1-[2-(1-methyl-1H-benzo[d]imidazol-2-yl)phenyl]methylidene-1-R,2,5-pyrrolidinediones 6a–f. A three-step mechanism including Michael addition, Diels–Alder reaction and skeletal rearrangement of tricyclic 7-azanorbornene derivatives 5a–f is proposed to explain the formation of the final products. An X-ray structure analysis of compound 6a shows the presence of a twisted double bond with a torsion angle of 6.42°. In the 1H NMR spectra the presence of a chirality center and axis in the adducts 6a–f implies the presence of atropodiastereomers.

Keywords: Atropisomerism, Diels–Alder reaction, cycloaddition, isoindolo[2,1-a]-benzimidazole, Michael addition

Introduction
The study of the chemical properties of isoindole derivatives is an important area in heterocyclic chemistry.1 Their most typical reaction is the [4+2]cycloaddition (Diels–Alder reaction), which is well studied for simple isoindoles.1b,c,2 In contrast, the reactions of the corresponding annulated derivatives with dienophiles are more complex and include not only Michael or Diels–Alder reactions but are also usually accompanied with original skeleton rearrangements.3

Among the other annulated isoindoles which are much more delocalized, the heterocyclic system of isoindolo[2,1-a]benzimidazole 2 occupies a special place.4 This is due to a weak interaction between the isoindolic and the benzimidazolic parts of the molecule. It was thus
interesting to study their reactions with dienophiles. Herein, we present the original reactions of the 5-methyl-5H-isoindolo[2,1-a]benzimidazole.5

Results and Discussion

The starting isoindole 2 was obtained in situ from the 5-methyl-5H-isoindolo[2,1-a]benzimidazolium iodide 1 using triethylamine as a base (Scheme 1). Reaction of 2 with two equivalents of p-tolylmaleimide leads to the compound 6a (71% yield). Its structure was proved by an X-Ray structure analysis (Figure 1). The analogous compounds (6b–f) were isolated in high yields (72–85%) in the reaction with other N-arylmaleimides, and completely identified by NMR-, mass-, IR- spectra and elemental analysis.

Scheme 1

The main feature concerning the X-ray result is that it permits to ascertain the proposed structural determination. Compound 6a crystallizes with one molecule of chloroform and we observe no noticeable intra or intermolecular short distances. The 5-membered ring C(2)–C(3)–C(4)–N(1)–C(5) in the crystal is nearly planar (no atom deflection from the root-mean-square plane > 0.02 Å) whereas the other succinimide ring C(13)–C(14)–C(15)–N(2)–C(16) present a slight envelope form with C(13) situated at 0.134 Å over the root-mean-square plane of the four
other atoms (no deflection > 0.02 Å). The tolyl substituents are staggered to the five membered rings (torsion angles are 50.66° for C(4)–N(1)–C(6)–C(11) and -70.42° for C(16)–N(2)–C(17)–C(22)) and quite parallel together. The double bond C(1)–C(2) is twisted (torsion angles C(24)–C(1)–C(2)–C(3) is 6.21°) and is therefore lengthened to 1.351 Å, while a standard double bond length is 1.322 Å. Apparently, this is due to the steric hindrances around the double bond.

Figure 1. Mercury 1.4.2 sticks drawing of the crystal structure of 6a.

To explain this unexpected reaction we propose below a probable mechanism. We postulate first a Michael-type reaction of the isoindole 2 with one equivalent of corresponding maleimide (3a–f), forming the succinimide derivative 4. The second step may be a Diels–Alder reaction of the intermediate 4 with the second equivalent of maleimide giving the 7-azanorbornene derivative 5. The latter rearranges in the isolated products 6a–f in one or more additional steps. This is associated to the destruction of two bonds in the strained cycle and the aromatization of the benzimidazole ring.

Interestingly, in spite of their great difference in electronic properties, similar products 8 were obtained in the reaction of pyrido[2,1-a]isoindole 7 with maleimides 3b,c (Scheme 2). In fact, 7 is a 14π-electron heteroaromatic system 4a,b in contrast to the 10π-electronic system of isoindolo[2,1-a]benzimidazole. But there is a weaker interaction between isoindole and the annulated benzimidazole fragments, 4c which makes it more similar to the 10π-electronic system of the simple isoindoles.
Thus, the observation of Michael adducts for pyrido[2,1-α]isoindole, using GC–MS and GC–UV spectra and the isolation of 7-azanorbornene derivatives in the reaction of isoindolo[2,1-α]quinazolin-5-one with maleimide derivatives (Scheme 3) can be considered as supplementary arguments for the proposed mechanism.

Spectroscopic properties of compounds 6a–f
The 1H NMR spectra of compounds 6a–f present more signals than expected from the formulae. Moreover, there is only one spot in TLC. This is due to the presence of two chiral elements in the compounds (Scheme 4) – a chiral axis (in bold) and chiral center (marked by an asterisk), which may lead up to four isomeric forms. Furthermore, after treating the products 6a–f with D2O we observe in the 1H- NMR spectra the exchange of a broad singlet near 6 ppm, which indicates the presence of an enol form (Scheme 4) in the reaction mixture. Thus, in all cases, we observed the signals of three isomers – two atropodiastereomers and one enol form. All signals in 1H- NMR spectra are assigned by 2D NMR and decoupling experiments. The spectra of the aliphatic part (2.00–5.00 ppm) of all adducts are similar and this spectral range will be described here for compound 6a.
Scheme 4

The two diastereomers (I, II) and the enol (III) of 6a are in the ratio 100:35:59 respectively. We show the most characteristic fragment in Figure 2. The doublet of doublets of proton Hc (II) is located at 2.60 ppm. The signal of the same proton Hc of the isomer I (Hc (I)) is at weaker field at 2.97 ppm. The doublet for proton Ha (I) ($J = 21.5$ Hz) is situated at 3.04 ppm. We observe the same value of coupling constant between Hc–Hb protons for all isomers (I, II, III) of 6a–f. The doublets of doublets of protons Hd of I and II isomers have similar chemical shifts (3.15 and 3.18 ppm respectively) and appears as a complicated multiplet. A doublet at 3.25 ppm with $J$ 21.5 Hz, mentioned before, correspond to the two Hb protons [Hb (I) and Hb (II)] according to their intensity. The next doublet at 3.38 ppm has also a $J$ of 21.5 Hz and corresponds to the Ha proton of isomer II. Obviously, the signals of Hc and Hd protons in enol III are doublets and not doublets of doublets as there is no Hc proton in the enol form. Two such doublets are observed at 3.44 and 3.48 ppm. All $^1$H NMR signals for compound 6a are summarized in the Table 1.

Figure 2. $^1$H- 400 MHz spectrum of 6a in CDCl$_3$ in the aliphatic range.
Similar spectra were also observed for compounds 8,3c with a pyridine instead of the benzimidazole ring. In this case, the existence of a diastereomeric mixture was proved using temperature-dependent NMR spectra3c in which the coalescence of signals took place with increasing the temperature, thus lowering the rotation barrier about the chiral bond.

Table 1. Chemical shifts and coupling constants in $^1$H NMR- spectra of compound 6a

| Proton  | Isomer I, $\delta$, (J, Hz) | Isomer II, $\delta$, (J, Hz) | Isomer III, $\delta$, (J, Hz) | Enol form |
|---------|----------------------------|-----------------------------|-----------------------------|-----------|
| Ar-CH$_3$ | 2.38 (s); 2.39 (s) | 2.34 (s); 2.43 (s) | 2.37 (s); 2.40 (s) |
| H$_a$    | 3.04 (d, 21.5)  | 3.38 (d, 21.5) | 3.95 (d, 21.5) |
| H$_b$    | 3.25 (d, 21.5)  | 3.25 (d, 21.5) | 3.70 (d, 21.5) |
| H$_c$    | 2.97 (dd, 6.7; 18.2) | 2.62 (dd, 5.9; 18.2) | 3.44 (d, 13.8) |
| H$_d$    | 3.15 (dd, 9.5; 18.2) | 3.18 (dd, 9.5; 18.2) | 3.48 (d, 13.8) |
| H$_e$    | 4.20 (m); 4.30 (t, 7.0) | 5.67 (br s) |
| N-CH$_3$ | 3.87 (s) | 3.81 (s) | 3.67 (s) |
| H$_A$Ar  | 6.94–7.81 (m) |

Conclusions

The reaction of 5-methyl-5$H$-isoindolo[2,1-a]benzimidazole with maleimide derivatives leads to rearranged products 6a–f in good yields. The proposed mechanism of the reaction begins by a Michael addition of one equivalent of maleimide to the isoindole followed by a Diels–Alder cycloaddition of the second equivalent of maleimide and subsequent rearrangement of the intermediate tricyclic 7-azanorbornene derivatives 5a–f. From X-ray structure analysis of compound 6a, it appears that the C–C- double bond is twisted (torsion angle 6.42°). A detailed analysis of NMR- spectra of compounds 6a–f shows the presence in solution of a mixture of two diastereomers and one enol form.

Experimental Section

**General Procedures.** Uncorrected melting points were measured by a Boetius–Thiele apparatus. IR spectra were recorded on a Perkin–Elmer 1760X FT–IR, the EI mass-spectra (70 eV) on a Nermag R10 at the “Service Commun de Spectrométrie de Masse” of the Paul Sabatier University Toulouse, and the $^{13}$C- and other NMR spectra on a Varian Mercury 400 (400 MHz) ($^1$H, 400 MHz, $^{13}$C, 100 MHz) in CDCl$_3$, $\delta$ values are given in ppm with TMS as internal standard. Elemental analysis were performed at the Department of Chemistry, Kyiv National Taras Shevchenko University.
3-\((E)\)-1-(2,5-Dioxo-1\(H\)-3-pyrrolyl)-1-[2-(1-methyl-1\(H\)-benzo[d]imidazol-2-yl)phenyl]methylidene-1\(R\)-2,5-pyrrolinediones (6a–f). To 60 mL of a hot ethanolic solution of 1 mmol (0.35 g) 5-methyl-5\(H\)-isoindolo[2,1-\(a\)]benzimidazolium iodide 1 (obtained according to the literature\(^8\)) and 2 mmol of the corresponding maleimide (3a–f) was added 2.5 mmol (0.25 g) of triethylamine. This solution was heated at reflux for 4 h and then evaporated in vacuo. The residue was purified by column chromatography (CH\(_2\)Cl\(_2\)/MeOH, 100:1).

3-\((E)\)-1-[2-(1-Methyl-1\(H\)-benzo[\(d\]]imidazol-2-yl)phenyl]-1-\([1-(4-methylphenyl)-2,5\)-dioxotetrahydro-1\(H\)-3-pyrrolyl\]methylidene-1-(4-methylphenyl)-2,5-pyrrolidinedione (6a). Treatment of 0.35 g (1 mmol) 5-methyl-5\(H\)-isoindolo[2,1-\(a\)]benzimidazolium iodide 1 and 0.37 g (2 mmol) N-\((p\)-tolyl)maleimide 3a according to the general procedure gave 0.42 g (0.71 mmol, 71\%) 6a as brown solid, mp: 139–141°C. IR (KBr): 3035 (w), 2950 (w), 2922 (m), 2866 (m), 1710 (s), 1514 (s), 1473 (m), 1456 (m), 1429 (m), 1380 (s), 1326 (m), 1282 (m), 1195 (s), 1141 (s), 1053 (m), 1022 (m), 1004 (m), 939 (w), 912 (m), 815 (m), 769 (m), 759 (m), 746 (m), 715 (m), 648 (m), 584 (m), 509 (cm\(^{-1}\)).

\(^{1}\)H NMR (400 MHz, CDCl\(_3\)): 2.34 (s, Ar-\(CH_3\) (II)), 2.37 (s, Ar-\(CH_3\) (III)), 2.38 (s, Ar-\(CH_3\) (I)), 2.40 (s, Ar-\(CH_3\) (I)), 2.43 (s, Ar-\(CH_3\) (II)), 2.62 (dd, \(J = 5.9, 18.2\) Hz, \(H_c\) (II)), 2.97 (dd, \(J = 6.7, 18.2\) Hz, \(H_c\) (I)), 3.04 (dd, \(J = 21.5\) Hz, \(H_e\) (I)), 3.15 (dd, \(J = 9.5, 18.2\) Hz, \(H_d\) (I)), 3.18 (dd, \(J = 9.5, 18.2\) Hz, \(H_d\) (II)), 3.25 (d, \(J = 21.5\) Hz, \(H_b\) (I, II)), 3.38 (d, \(J = 21.5\) Hz, \(H_b\) (II)), 3.44 (d, \(J = 13.8\) Hz, \(H_c\) (III)), 3.48 (d, \(J = 13.8\) Hz, \(H_d\) (III)), 3.67 (s, N-\(CH_3\) (III)), 3.70 (d, \(J = 21.5\) Hz, \(H_b\) (III)), 3.81 (s, N-\(CH_3\) (I)), 3.95 (d, \(J = 21.5\) Hz, \(H_a\) (III)), 4.20 (m, \(H_e\) (I)), 4.30 (t, \(J = 7.0\) Hz, \(H_e\) (II)), 5.67 (br s, \(H_e\) (III)), 6.94–7.81 (m, Harom) ppm. Ratio I:II:III = 100:35:59. \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): 21.21, 31.45, 34.11, 34.71, 34.20, 34.44, 37.43, 47.84, 61.85, 109.69, 109.85, 109.94, 119.80, 120.16, 120.28, 122.68, 122.93, 123.35, 123.45, 126.16, 126.20, 126.84, 128.17, 128.52, 129.22, 129.61, 129.76, 129.84, 129.96, 130.42, 130.90, 131.14, 131.16, 135.90, 138.55, 138.67, 142.76, 148.84, 151.11, 172.25, 172.35, 175.78, 175.97 ppm. MS (EI, 70 eV): m/z (%) = 594 (16.28) [M]+, 432 (15.49), 406 (100.00), 299 (3.77), 246 (25.37), 133 (7.05), 107 (11.66), 55 (4.91). Anal. Calcd. for C\(_{37}\)H\(_{30}\)N\(_4\)O\(_4\): C 74.73, H 5.08, N 9.42. Found C 74.80, H 5.12, N 9.50.

X-Ray crystal structure analysis of 6a
The X-ray structure determination was performed at room temperature (298 K) for 2a on a Nonius Kappa CCD diffractometer with a graphite oriented monochromator utilizing MoK\(_\alpha\) radiation (\(\lambda=0.71073\)). The structure was solved by direct methods and refined by least-squares procedures. All diagrams and Calculations were performed using maXus package programs (Mac Science, Japan). The crystals of compound 6a are triclinic (C\(_{37}\)H\(_{30}\)N\(_4\)O\(_4\); CHCl\(_3\)). a=10.947(2) Å, b=11.5051(8) Å, c=15.376(5) Å, \(\alpha=70.40(2)^\circ\), \(\beta=77.77(3)^\circ\), \(\gamma=82.932(15)^\circ\), \(V=1780.1(7)\) Å\(^3\), \(d=1.332\)g/cm\(^3\), space group P1 (bar), Z=2. Intensities of 2776 unique reflections (R=0.064; \(R_w=0.121\)) were measured.
The crystallographic data submission CCDC 637008 contains the supplementary crystallographic data for 6a. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

1-(4-Methoxyphenyl)-3-(E)-1-[1-(4-methoxyphenyl)-2,5-dioxotetrahydro-1H-3-pyrrolyl]-1-[2-(1-methyl-1H-benzo[d]imidazol-2-yl)phenyl]methylidene-2,5-pyrrolidinedione (6b). Compound 6b was obtained from 0.35 g (1 mmol) 5-methyl-5H-isouindolo[2,1-a]benzimidazolium iodide 1 and 0.41 g (2 mmol) N-(p-anisyl)maleimide 3b according to the general procedure in 85% yield (0.50 g, 0.85 mmol) as a brown solid, mp: 137–138°C. IR (KBr): 3091 (m), 3057 (w), 2947 (w), 1710 (s), 1654 (m), 1490 (s), 1458 (m), 669 (w), 649 (m), 543 (w), 505 (m) cm⁻¹. ¹H NMR (400 MHz, CDCl₃): 2.61 (dd, J = 5.0, 18.3 Hz, H₆ (II)), 2.94 (dd, J = 6.9, 18.3 Hz, H₆ (I)), 2.98 (d, J = 21.5 Hz, H₄ (I)), 3.16 (d, J = 8.5 Hz, H₄ (I*)), 3.10 (d, J = 9.4 Hz, H₄ (II*)), 3.21 (d, J = 21.5 Hz, H₄ (I, II)), 3.33 (d, J = 21.5 Hz, H₄ (II)), 3.39 (d, J = 13.7 Hz, H₄ (III)), 3.43 (d, J = 13.7 Hz, H₆ (III)), 3.69 (d, J = 21.5 Hz, H₆ (III)), 3.73 (d, J = 21.5 Hz, H₆ (I)), 3.76 (CH₂), 3.78 (CH₂), 3.79 (CH₃), 3.80 (CH₃), 3.81 (CH₃), 3.81 (CH₃), 3.84 (CH₃), 4.17 (t, J = 8.0 Hz, H₂ (I)), 4.27 (t, J = 7.2 Hz, H₂ (II)), 5.69 (br s, H₆ (III)), 6.87–7.84 (m, H₅ arom) ppm. Ratio I:II:III = 100:29:62; III is the enol form. ¹³C NMR (100 MHz, CDCl₃): 24.53, 31.43, 34.06, 35.15, 37.41, 43.82, 55.48, 109.36, 110.85, 110.33, 114.27, 114.39, 114.44, 114.61, 120.18, 120.30, 122.72, 122.96, 123.38, 123.48, 123.58, 123.60, 123.64, 123.81, 123.85, 124.57, 125.14, 125.17, 126.74, 126.78, 126.81, 126.84, 126.96, 129.22, 129.96, 130.44, 130.60, 130.95, 135.88, 135.97, 142.77, 159.43, 159.52, 167.78, 172.36, 172.45, 175.96, 176.13 ppm. MS (EI, 70 eV): m/z (%) = 626 (60.10) [M]+, 476 (6.25), 422 (100.00), 4.06 (5.73), 299 (6.13), 246 (26.26), 205 (6.68), 123 (13.01), 108 (10.31), 55 (3.15). Anal. Calcd. for C₇₃H₇₄N₄O₆: C 70.92, H 4.83, N 8.94. Found C 71.20, H 5.01, N 9.10.

1-(4-Bromophenyl)-3-(E)-1-[1-(4-bromophenyl)-2,5-dioxotetrahydro-1H-3-pyrrolyl]-1-[2-(1-methyl-1H-benzo[d]imidazol-2-yl)phenyl]methylidene-2,5-pyrrolidinedione (6c). Treatment of 0.35 g (1 mmol) 5-methyl-5H-isouindolo[2,1-a]benzimidazolium iodide 1 and 0.50 g (2 mmol) N-(p-bromophenyl)maleimide 3c gave 6c (0.58g, 0.80 mmol, 80%) as a brown solid, mp: 149–150°C. IR (KBr): 3091 (m), 3057 (w), 2947 (w), 1710 (s), 1654 (m), 1490 (s), 1458 (m), 1429 (m), 1379 (s), 1328 (m), 1280 (m), 1193 (m), 1178 (m), 1139 (m), 1097 (m), 1070 (m), 1031 (w), 1012 (s), 937 (w), 910 (m), 823 (m), 800 (m), 773 (m), 765 (m), 746 (m), 711 (m), 669 (w), 649 (m), 634 (m), 543 (w), 505 (m) cm⁻¹. ¹H NMR (400 MHz, CDCl₃): 2.68 (dd, J = 5.2, 18.3 Hz, H₆ (II)), 2.94 (dd, J = 6.8, 17.3 Hz, H₆ (I)), 2.97 (d, J = 21.5 Hz, H₂ (I)), 3.14 (dd, J = 9.5, 18.3 Hz, H₆ (I)), 3.19 (dd, J = 7.1, 17.3 Hz, H₆ (II)), 3.20 (d, J = 21.5 Hz, H₂ (I, II)), 3.34 (d, J = 21.5 Hz, H₂ (I)), 3.39 (d, J = 12.7 Hz, H₂ (II)), 3.40 (d, J = 12.7 Hz, H₂ (III)), 3.48 (d, J = 21.5 Hz, H₂ (III)), 3.50 (d, J = 21.5 Hz, H₂ (III)), 3.65 (N=CH₃ (III)), 3.77 (N=CH₃ (II)), 3.85 (N=CH₃ (I)), 4.18 (t, J = 8.0 Hz, H₂ (I)), 4.28 (t, J = 8.0 Hz, H₂ (II)), 5.59 (br s, H₂ (III)), 6.89–8.10 (m, H₅ arom) ppm. Ratio I:II:III = 100:52:30; III is the enol form. ¹³C NMR (100 MHz, CDCl₃): 23.31, 31.46, 35.16, 37.48, 44.17, 47.89, 53.47, 109.72, 109.91, 120.17, 120.31, 122.31,
122.50, 122.82, 122.06, 123.52, 123.61, 127.85, 127.89, 127.95, 128.05, 128.10, 128.28, 128.57, 128.70, 130.28, 130.45, 130.64, 130.99, 131.25, 132.12, 132.25, 132.26, 132.31, 132.51, 135.98, 142.82, 167.34, 171.62, 175.14, 175.38, 176.62 ppm. MS (EI, 70 eV): m/z (%) = 723 (20.63) [M]+, 571 (0.65), 470 (100.00), 391 (4.52), 271 (20.90), 246 (24.83), 171 (7.96), 113 (28.15), 55 (10.05). Anal. Calcd. for C₃₅H₂₄Br₂N₄O₄: C 58.03, H 3.34, N 7.73. Found C 58.20, H 3.42, N 7.94%.

1-(4-Chlorophenyl)-3-(E)-1-[1-(4-chlorophenyl)-2,5-dioxotetrahydro-1H-3-pyrrolyl]-1-[2-(1-methyl-1H-benzo[d]imidazol-2-yl)phenyl]methylidene-2,5-pyrrolidinedione (6d).

Treatment of 5-methyl-5H-is indolo[2,1-α]benzimidazolium iodide 1 (0.35 g, 1 mmol) and 0.42 g (2 mmol) of N-(p-chlorophenyl)maleimide 3d produced 6d (0.44 g, 0.69 mmol, 69%) as a brown solid, mp 130–132°C. IR (KBr): 3095 (w), 3057 (w), 2979 (w), 2947 (w), 1712 (s), 1651 (m), 1614 (m), 1595 (m), 1531 (m), 1492 (s), 1458 (m), 1429 (m), 1379 (s), 1326 (m), 1282 (m), 1244 (m), 1191 (s), 1141 (s), 1089 (s), 1055 (m), 1031 (m), 1016 (s), 937 (m), 912 (m), 825 (s), 765 (s), 746 (s), 713 (m), 649 (m), 507 (m), 470 (w), 418 (m) cm⁻¹. ¹H NMR (400 MHz, CDCl₃): 2.69 (dd, J = 5.6, 18.2 Hz, H_e (II)), 2.95 (dd, J = 7.3, 18.7 Hz, H_a (I)), 2.96 (d, J = 21.5 Hz, H_a (I)), 3.14 (dd, J = 9.6 Hz, H_d (I)*), 3.21 (d, J = 9.8 Hz, H_d (II)*), 3.22 (d, J = 21.5 Hz, H_b (I, II)), 3.34 (d, J = 21.5 Hz, H_b (II)), 3.40 (br s, H_c (II)), 3.49 (d, J = 21.5 Hz, H_b (III)), 3.60 (d, J = 21.5 Hz, H_a (III)), 3.70 (N–CH₃ (III)), 3.78 (N–CH₃ (II)), 3.85 (N–CH₃ (I)), 4.18 (m, H_e (I, II)), 5.59 (br s, H_e (III)), 6.78–8.06 (m, H_arom) ppm. Ratio I:II:III = 100:58:30. ¹³C NMR (100 MHz, CDCl₃): 18.30, 31.49, 35.12, 37.48, 47.30, 47.84, 53.43, 109.40, 109.76, 109.88, 109.98, 120.12, 120.23, 120.52, 122.77, 123.02, 123.47, 123.58, 123.87, 127.20, 127.20, 127.25, 127.55, 127.75, 128.05, 128.26, 128.69, 128.83, 129.13, 129.22, 129.26, 129.32, 129.60, 129.71, 130.60, 130.98, 134.39, 166.42, 170.25, 171.68, 175.30 ppm. MS (EI, 70 eV): m/z (%) = 634 (12.75) [M]+, 526 (4.48), 426 (100.00), 299 (4.21), 246 (29.03), 206 (8.11), 127 (25.43), 113 (17.03), 55 (5.97). Anal. Calcd. for C₃₅H₂₄Br₂N₄O₄: C 66.15, H 3.81, N 8.82. Found C 66.25, H 4.06, N 8.96.

3-(E)-1-[2-(1-Methyl-1H-benzo[d]imidazol-2-yl)phenyl]-1-[1-(3-nitroph enyl)-2,5-dioxotetrahydro-1H-3-pyrrolyl]methylidene-1-(3-nitroph enyl)-2,5-pyrrolidinedione (6e).

Treatment of 5-methyl-5H-is indolo[2,1-α]benzimidazolium iodide 1 (0.35 g, 1 mmol) and N-(m-nitrophenyl)maleimide 3e (0.44 g, 2 mmol) gave 6e (0.47 g, 0.72 mmol, 72%) as a brown solid, mp 128–130°C. IR (KBr): 3089 (w), 3057 (w), 2976 (w), 2945 (w), 2869 (w), 1714 (s), 1614 (m), 1600 (m), 1531 (s), 1481 (m), 1461 (m), 1431 (m), 1379 (s), 1350 (s), 1296 (m), 1284 (m), 1245 (m), 1197 (s), 1178 (s), 1093 (m), 1056 (m), 1029 (m), 1004 (m), 948 (m), 931 (w), 889 (m), 858 (w), 821 (m), 802 (m), 767 (m), 738 (s), 675 (m), 642 (m), 619 (m), 595 (m), 578 (m), 543 (w), 522 (w), 516 (w), 484 (m) cm⁻¹. ¹H NMR (400 MHz, CDCl₃): 2.87 (dd, J = 6.0, 14.0 Hz, H_e (II)), 3.01 (dd, J = 6.9, 18.3 Hz, H_c (I)), 3.02 (d, J = 21.5 Hz, H_a (I)), 3.23 (d, J = 10.1 Hz, H_d (I)*), 3.29 (d, J = 10.1 Hz, H_d (II)*), 3.35 (d, J = 21.5 Hz, H_b (I, II)), 3.41 (d, J = 21.5 Hz, H_a (II)), 3.50 (m, H_e (III)), 3.46 (m, H_d (III)), 3.58 (d, J = 21.5 Hz, H_a (III)), 3.69 (d, J = 21.5 Hz, H_e (III)), 3.72 (N–CH₃ (I)), 3.84 (N–CH₃ (III)), 3.90 (N–CH₃ (II)), 4.21 (m, H_e (II)), 4.26 (m, H_e (I)), 5.48 (br s, H_e (III)), 7.18–8.29 (m, H_arom) ppm. Ratio I:II:III = 100:54:30. ¹³C NMR (100 MHz, CDCl₃): 20.24, 31.24, 31.53, 34.12, 109.44, 109.85, 109.99, 118.63, 120.77, 120.46.
121.52, 122.27, 122.84, 123.08, 123.31, 123.93, 128.71, 128.77, 129.83, 130.07, 140.26, 131.72, 132.13, 132.27, 133.93, 148.35, 165.94, 168.77, 171.22, 172.18, 174.87 ppm. MS (EI, 70 eV): m/z (%) = 656 (4.92) [M]+, 437 (32.48), 391 (4.10), 319 (12.48), 246 (62.60), 218 (30.12), 138 (100.00), 92 (87.99), 54 (12.67). Anal. Calcd. for C_{35}H_{24}N_{6}O_{8}: C 64.02, H 3.68, N 12.80. Found C 64.30, H 3.86, N 13.14%.

3-((E)-1-(2,5-Dioxo-1-phenyltetrahydro-1H-3-pyrrolyl)-1-[2-(1-methyl-1H-benzo[d]-imidazol-2-yl)phenyl]methylidene-1-phenyl-2,5-pyrrolidinedione (6f). Treatment of 5-methyl-5H-isoindolo[2,1-a]benzimidazolium iodide 1 (0.35g, 1 mmol) and N-phenyl-maleimide 3f (0.35 g, 2 mmol) gave 6f (0.48g, 0.85 mmol, 85%) as a brown solid, mp 135–136°C. IR (KBr): 3060 (w), 3001 (w), 2947 (w), 1708 (s), 1656 (m), 1597 (m), 1560 (w), 1543 (w), 1535 (w), 1498 (s), 1456 (m), 1438 (m), 1429 (m), 1379 (s), 1326 (m), 1282 (m), 1265 (m), 1244 (m), 1191 (s), 1141 (s), 1099 (m), 1072 (m), 1053 (m), 1029 (m), 1004 (m), 937 (m), 910 (m), 823 (m), 804 (m), 746 (s), 694 (s), 669 (m), 644 (m), 619 (m), 541 (m), 503 (m). 1H NMR (400 MHz, CDCl3): 2.63 (dd, J = 5.4, 18.9 Hz, Hc (II)), 2.97 (dd, J = 7.1, 18.4 Hz, Hc (I)), 3.00 (d, J = 21.5 Hz, Ha (I)), 3.11 (d, J = 9.6 Hz, Hd (I)*), 3.17 (d, J = 10.5 Hz, Hd (II)*), 3.23 (d, J = 21.5 Hz, Hb (I, II)), 3.35 (d, J = 21.5 Hz, Hb (II)), 3.43 (d, J = 11.0 Hz, Hc (III)), 3.47 (d, J = 11.0 Hz, Hd (III)), 3.54 (d, J = 21.5 Hz, Hb (III)), 3.58 (d, J = 21.5 Hz, Ha (III)), 3.64 (N–CH3 (III)), 3.77 (N–CH3 (II)), 4.20 (m, Hc (I)), 4.28 (m, Ha (II)), 5.71 (br s, Hb (III)), 6.97–7.81 (m, H_{a_{rom}}) ppm. Ratio I:II:III = 100:66:37. 13C NMR (100 MHz, CDCl3): 31.38, 31.44, 34.14, 34.77, 35.21, 37.41, 43.90, 47.35, 47.64, 47.83, 53.48, 109.75, 109.88, 109.97, 119.79, 120.14, 120.27, 120.46, 122.21, 122.74, 122.96, 123.39, 123.49, 123.90, 124.30, 126.36, 126.40, 126.58, 127.05, 127.25, 128.17, 128.59, 128.68, 128.98, 128.99, 129.09, 129.31, 130.62, 130.92, 131.18, 132.50, 135.89, 135.97, 149.04, 167.59, 168.06, 172.10, 175.10, 175.60, 175.81 ppm. MS (EI, 70 eV): m/z (%) = 656 (20.37) [M]+, 418 (16.85), 392 (100.00), 271 (16.05), 246 (19.89), 93 (7.70). Anal. Calcd. for C_{35}H_{26}N_{4}O_{4}: C 74.19, H 4.63, N 9.89. Found C 74.32, H 4.90, N 10.11.

* The resolution was worse than in the case of 6a, and only two (instead of four) signals were observed.

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