New method for the synthesis of β-tropolones: structures of condensation products of *o*-quinones with 2-methylquinolines and the mechanism of their formation*

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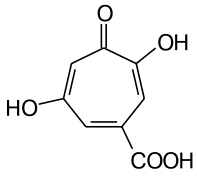
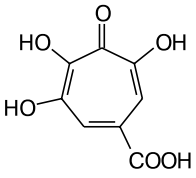
A new method was developed for the synthesis of functionalized β-tropolones based on acid-catalyzed condensation of 2-methylquinoline derivatives with 3,5-di(*tert*-butyl)-1,2-benzoquinone and 4,6-di(*tert*-butyl)-3-nitro-1,2-benzoquinone (**14**). The mechanism of the multistep reaction giving rise to β-tropolones and their tautomerism were studied by quantum chemical methods (DFT B3LYP/6-31G**). The reaction of 2-methylquinoline derivatives containing the tertiary amino group at position 4 with quinone **14** is accompanied by the formation of derivatives of a new heterocyclic system, *viz.*, 4,6-dioxo-2-azabicyclo[3.3.0]octa-2,7-diene *N*-oxide. The molecular and crystal structures of two 5,7-di(*tert*-butyl)-3-hydroxy-2-(quinolin-2-yl)tropolones and two dioxoazabicyclooctadiene *N*-oxides, as well as of the preparatively isolated intermediate of the first condensation step and of the by-product of the reaction were established by X-ray diffraction.

Key words: β-tropolones, intramolecular hydrogen bond, quantum chemical calculations, X-ray diffraction study, tautomerism.

Due to the unique structure and properties of the seven-membered tropolone ring and a broad spectrum of biological activities, natural compounds of the tropolone series (colchicine, colchamine, α-, β-, and γ-thujaplicins, *etc.*) and their synthetic analogs have attracted considerable attention.[1] Most of the already-known tropolones belong to α-tropolones, *i.e.*, 2-hydroxytropone derivatives. β-Tropolones (3-hydroxytropones) are much less studied, although they include biologically active compounds, such as stipitatic acid (**1**) and puberulic acid (**2**).



1



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The latter fact is primarily because convenient procedures for the synthesis of β-tropolone derivatives are lacking. Unsubstituted β-tropolone isolated as picrate was prepared for the first time in very low yield by decarboxylation of 3,5-dimethoxycyclohepta-1,3,5-trienecarboxylic acid followed by bromination of the resulting 3,5-dimethoxycycloheptatriene giving rise to β-methoxytropone and demethylation of the latter.[2] A more general approach to the synthesis of β-tropolone derivatives is based on the multistep transformation of 3,4,5-trimethoxybenzoic acid involving its reduction to 3,5-dimethoxy-1,4-dihydrobenzyl alcohol, the preparation of its tosyl derivative, and the formation of a mixture of 1,3-dimethoxycycloheptatrienes (as a result of thermal expansion of the six-membered ring) followed by their oxidation.[3] Unsubstituted β-tropolone was also prepared by photooxygenation of cyclohepta-1,3,5-triene with singlet oxygen followed by methanolysis of the resulting isomeric en-

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doperoxides giving rise to 1,2-dihydro-3-hydroxytropone and oxidation of the latter with chromium oxide.[4] β-Tropolone derivatives containing substituents in the vicinal position with respect to both functional groups are preparatively more accessible and more interesting in view of their biological properties. 2-Carboxy-β-tropolones were synthesized in low yields by a series of transformations based on condensation of diazoacetic ester with 1,2-dimethoxybenzene or 1,2,4-trimethoxybenzene.[5,6] Recently, a more convenient four-step method has been developed based on the cycloaddition reaction of 2-methylfuran with symmetrical tetrachloroacetone producing 2-alkoxy-β-tropolones in 20—37% yields.[7] 2-Acyl-β-tropolones were synthesized in moderate yields (12—66%) by the reactions of *in situ* generated triphenylbismuthonium ylides with *o*-quinones.[8] The reaction of tetrachloro-*o*-benzoquinone with acetone also produces β-tropolone derivatives.[9] Earlier, the structure of an α-tropolone derivative has been assigned to this reaction product.[10]

In the present study, we developed a new general method for the synthesis of β-tropolone derivatives based on acid-catalyzed condensation of *o*-quinones with 2-methylquinolines. The structures and the mechanism of formation of the major reaction products, intermediates, and by-products were studied by X-ray diffraction and quantum chemical methods.

Results and Discussion

Synthesis and structures of 5,7-di(*tert*-butyl)-3-hydroxy-2-(quinolin-2-yl)tropones. The reactions of carbonyl compounds with methylene-active substrates are among the most widely used methods for the carbon—carbon bond formation.[11] However, the behavior of quinones in these transformations is poorly known. Earlier, we have found[12] that when fusing 3,5-di(*tert*-butyl)-1,2-benzoquinone (**3**) with 2-methylquinolines **4** in the presence of *p*-toluenesulfonic acid at 160—170 °C (method ***A***) or refluxing their solution in *o*-xylene for 3—6 h (method ***B***), 2-(quinolin-2-yl)-β-tropolones **6** (Scheme 1) instead of the expected aldol condensation products, *viz.*, *o*-methylenequinones **5**, were prepared in 7—43% yields. The highest yields were achieved with the use of a twofold excess of quinone **3**, which acts as an oxidizing agent in the final step of the transformation (Scheme 2).

In the present study, we demonstrated that condensation of *o*-quinones with 2-methylquinolines can be performed under milder conditions (storage of a solution of the components in acetic acid at room temperature for 1—4 days, method ***C***), β-tropolones **6** and **7** being prepared in substantially higher yields. The structures of compounds **6** and **7** were confirmed by ^{1}H NMR and IR spectroscopy and mass spectrometry (Tables 1—4). The molecular structures of β-tropolones (**6e** and **7a**) were established by X-ray diffraction (Figs 1 and 2, Table 5).

X-ray diffraction study demonstrated that compounds **6e** and **7a** exist as *s-cis* conformers with respect to the C(2)—C(8) bond. This conformation provides the formation of exclusively stable intramolecular O—H...N (see Fig. 1) or O...H—N hydrogen bonds (see Fig. 2). The O...N distances in compounds **6e** and **7a** are more than 0.5 Å shorter than the corresponding van der Waals contact and are the shortest bonds in all known systems with this type of intramolecular hydrogen bonds.[13,14] The hydrogen nuclei involved in intramolecular hydrogen bonds in compounds **6e** and **7a** are strongly deshielded and are observed in the ^{1}H NMR spectra at very low field (at δ 18—20, see Table 2). These values are comparable with the chemical shifts (19.1—19.7 ppm) of the protons of conjugated acids of proton sponges.[15] It is known[14,15]

Scheme 1

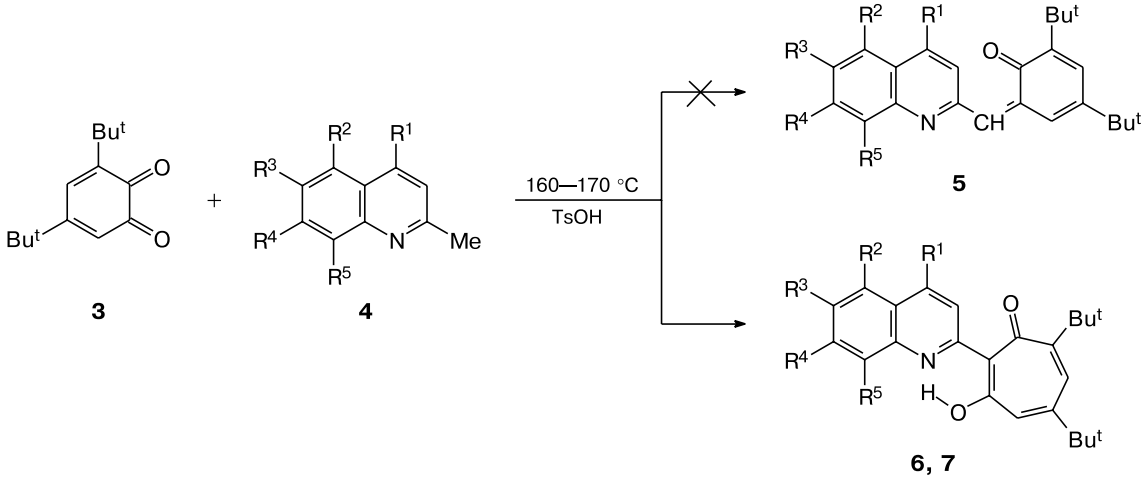
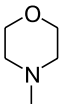
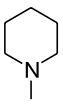


Table 1. Yields, melting points, and elemental analysis data for 5,7-di(*tert*-butyl)-3-hydroxy-2-(quinolin-2-yl)tropones **6** and **7**

Compound	R^1	R^2	R^3	R^4	R^5	Yield (%) Method	M.p. /°C	Found / Calculated (%) C	H	Cl	N	Molecular formula
6a	H	H	H	H	H	10(***B***)	126—128	79.61 79.74	7.40 7.53	—	3.72 3.87	$C_{24}H_{27}NO_2$
6b	H	NO_2	H	H	H	37(***C***)	172—174	70.74 70.92	6.33 6.45	—	7.02 6.89	$C_{24}H_{26}N_2O_4$
6c	Me	H	H	H	NO_2	11(***B***)	223—225	71.54 71.41	6.73 6.71	—	6.82 6.66	$C_{25}H_{28}N_2O_4$
6d	Cl	H	H	7,8-Benzo		11(***B***)	173—175	75.31 75.41	6.32 6.33	7.84 7.95	3.06 3.14	$C_{28}H_{28}ClNO_2$
6e	Cl	H	H	H	Me	11(***A***), 23(***B***), 60(***C***)	189—191	73.22 73.25	6.71 6.88	8.62 8.65	3.44 3.42	$C_{25}H_{28}ClNO_2$
6f	Cl	H	Me	H	Me	15(***A***), 26(***B***), 70(***C***)	198—201	73.61 73.66	7.02 7.08	8.12 8.36	3.20 3.30	$C_{26}H_{30}ClNO_2$
6g	Cl	H	H	Me	Me	12(***A***), 24(***B***), 63(***C***)	174—176	73.58 73.66	7.07 7.13	8.14 8.36	3.14 3.30	$C_{26}H_{30}ClNO_2$
6h	Cl	H	OMe	H	H	13(***B***)	157—159	70.56 70.49	6.72 6.63	8.48 8.32	3.40 3.29	$C_{25}H_{28}ClNO_3$
6i	Cl	NO_2	H	H	Me	11(***A***), 20(***B***)	210—212	65.93 66.00	5.92 5.98	7.84 7.79	6.03 6.16	$C_{25}H_{27}ClN_2O_4$
6j	Cl	NO_2	Me	H	Me	13(***A***), 21(***B***)	223—225	66.64 66.59	6.21 6.23	7.40 7.56	5.92 5.97	$C_{26}H_{29}ClN_2O_4$
6k	Cl	NO_2	H	Me	Me	11(***A***), 22(***B***), 43(***C***)	234—236	66.62 66.59	6.13 6.23	7.52 7.56	5.93 5.97	$C_{26}H_{29}ClN_2O_4$
7a		H	H	H	Me	34(***B***), 89(***D***)	200—202	75.52 75.62	7.72 7.88	—	5.99 6.08	$C_{29}H_{36}N_2O_3$
7b		H	Me	H	Me	26(***B***), 92(***D***)	222—224	75.94 75.92	7.95 8.07	—	5.81 5.90	$C_{30}H_{38}N_2O_3$
7c		H	H	Me	Me	29(***B***), 95(***D***)	227—229	75.84 75.92	7.99 8.07	—	5.93 5.90	$C_{30}H_{38}N_2O_3$
7d		H	OMe	H	H	94(***D***)	187—189	73.14 73.08	7.55 7.61	—	5.98 5.88	$C_{29}H_{36}N_2O_4$
7e		H	H	7,8-Benzo		89(***D***)	211—213	77.47 77.39	7.25 7.31	—	5.71 5.64	$C_{32}H_{36}N_2O_3$
7f		NO_2	H	H	Me	26(***B***), 88(***D***)	272—274	68.87 68.89	6.88 6.98	—	8.26 8.31	$C_{29}H_{35}N_3O_5$
7g		NO_2	Me	H	Me	24(***B***), 76(***D***)	203—205	69.33 69.34	7.07 7.18	—	8.11 8.09	$C_{30}H_{37}N_3O_5$
7h		NO_2	H	Me	Me	22(***B***), 86(***D***)	264—266	69.30 69.34	7.10 7.18	—	8.05 8.09	$C_{30}H_{37}N_3O_5$
7i		H	H	H	Me	6(***B***), 96(***D***)	144—146	78.48 78.56	8.17 8.35	—	6.13 6.11	$C_{30}H_{38}N_2O_2$
7j		H	Me	H	Me	81(***D***)	191—193	78.55 78.77	8.47 8.53	—	6.18 5.93	$C_{31}H_{40}N_2O_2$
7h		H	H	Me	Me	8(***B***), 86(***D***)	169—171	78.80 78.77	8.41 8.53	—	5.81 5.93	$C_{31}H_{40}N_2O_2$
7l		NO_2	H	H	Me	10(***B***), 74(***D***)	244—246	71.48 71.54	7.27 7.40	—	8.54 8.34	$C_{30}H_{37}N_3O_4$
7m		NO_2	Me	H	Me	8(***B***), 82(***D***)	198—200	71.79 71.93	7.41 7.59	—	8.02 8.12	$C_{31}H_{39}N_3O_4$

(*to be continued*)

Table 1 (*continued*)

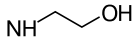
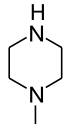
Compound	R^1	R^2	R^3	R^4	R^5	Yield (%) Method	M.p. /°C	Found / Calculated (%) C	H	Cl	N	Molecular formula
7n		NO_2	H	Me	Me	10(***B***), 78(***D***)	223—225	71.85 71.93	7.47 7.59	—	8.03 8.12	$C_{31}H_{39}N_3O_4$
7o		H	H	H	Me	94(***D***)	264—265	74.55 74.62	7.47 7.89	—	6.63 6.45	$C_{27}H_{34}N_2O_3$
7p		H	Me	H	Me	95(***D***)	238—240	74.75 74.97	7.97 8.09	—	6.53 6.24	$C_{28}H_{36}N_2O_3$
7q		H	H	Me	Me	98(***D***)	270—272	74.86 74.97	7.91 8.09	—	6.38 6.24	$C_{28}H_{36}N_2O_3$
7r		H	H	H	Me	93(***D***)	162—164	75.86 75.78	7.96 8.11	—	9.38 9.14	$C_{29}H_{37}N_3O_2$
7s		H	Me	H	Me	93(***D***)	190—192	75.96 76.07	8.16 8.30	—	9.18 8.87	$C_{30}H_{39}N_3O_2$
7t		H	H	Me	Me	90(***D***)	194—195	76.02 76.07	8.12 8.30	—	9.06 8.87	$C_{30}H_{39}N_3O_2$
7u	$NHC_6H_3(OMe)_2$-2,5	H	H	H	Me	9(***B***)	235—237	75.33 75.26	7.17 7.27	—	5.23 5.32	$C_{33}H_{38}N_2O_4$
7v	NHC_6H_4Me-4	NO_2	H	Me	Me	7(***B***)	220—222	73.54 73.44	6.73 6.91	—	7.82 7.79	$C_{33}H_{37}N_3O_4$
7w		NO_2	Me	H	Me	7(***B***), 74(***D***)	262—264	69.32 69.58	6.21 6.44	—	11.29 11.19	$C_{29}H_{32}N_4O_4$
7x		H	H	H	Me	84(***D***)	190—191	76.32 76.16	7.01 7.08	—	9.49 9.52	$C_{28}H_{31}N_3O_2$
7y		H	Me	H	Me	86(***D***)	191—193	76.22 76.45	7.14 7.30	—	9.39 9.22	$C_{29}H_{33}N_3O_2$
7z		H	H	Me	Me	93(***D***)	204—206	76.34 76.45	7.18 7.30	—	9.43 9.22	$C_{29}H_{33}N_3O_2$

Table 2. ^{1}H NMR spectroscopic data for 5,7-di(*tert*-butyl)-3-hydroxy-2-(quinolin-2-yl)tropones **6** and **7**

Compound	δ (*J*/Hz)
6a	1.25 (s, 9 H, Bu^t(5)); 1.39 (s, 9 H, Bu^t(7)); 6.62 (d, 1 H, H(4), *J* = 1.5); 6.69 (d, 1 H, H(6), *J* = 1.5); 7.44—8.18 (m, 6 H, quinoline); 19.3 (br.s, 1 H, C(3)OH)
6b	1.27 (s, 9 H, Bu^t(5)); 1.41 (s, 9 H, Bu^t(7)); 6.67 (d, 1 H, H(4), *J* = 1.7); 6.82 (d, 1 H, H(6), *J* = 1.7); 7.78 (t, 1 H, H(7′)); 8.15 (d, 1 H, H(3′), *J* = 8.4); 8.24—8.30 (m, 2 H, H(6′), H(8′)); 8.89 (d, 1 H, H(4′), *J* = 8.4); 18.25 (s, 1 H, C(3)OH)
6c	1.25 (s, 9 H, Bu^t(5)); 1.39 (s, 9 H, Bu^t(7)); 2.72 (s, 3 H, Me(4′)); 6.71 (d, 1 H, H(4), *J* = 1.7); 6.73 (d, 1 H, H(6), *J* = 1.7); 7.56 (t, 1 H, H(6′)); 8.05 (s, 1 H, H(3′)); 8.19 (d, 1 H, H(5′), *J* = 8.0); 8.43 (d, 1 H, H(7′), *J* = 8.0); 17.96 (s, 1 H, C(3)OH)
6d	1.30 (s, 9 H, Bu^t(5)); 1.44 (s, 9 H, Bu^t(7)); 6.77 (d, 1 H, H(4), *J* = 1.76); 6.84 (d, 1 H, H(6), *J* = 1.76); 7.7—8.9 (m, 6 H, arom.); 8.41 (s, 1 H, H(3′)); 19.35 (s, 1 H, C(3)OH)
6e	1.24 (s, 9 H, Bu^t(5)); 1.37 (s, 9 H, Bu^t(7)); 2.72 (s, 3 H, Me(8′)); 6.65 (d, 1 H, H(4), *J* = 1.7); 6.72 (d, 1 H, H(6), *J* = 1.7); 7.41 (t, 1 H, H(6′), *J* = 7.7); 7.54 (d, 1 H, H(7′), *J* = 7.6); 7.95 (d, 1 H, H(5′), *J* = 7.6); 8.23 (s, 1 H, H(3′)); 19.12 (s, 1 H, C(3)OH)

(*to be continued*)

Table 2 (*continued*)

Compound	δ (*J*/Hz)
6f	1.23 (s, 9 H, Bu^t(5)); 1.37 (s, 9 H, Bu^t(7)); 2.51 (s, 3 H, Me(6′)); 2.68 (s, 3 H, Me(8′)); 6.65 (d, 1 H, H(4), *J* = 1.88); 6.73 (d, 1 H, H(6), *J* = 1.88); 7.43 (s, 1 H, H(7′)); 7.78 (s, 1 H, H(5′)); 8.23 (s, 1 H, H(3′)); 19.19 (s, 1 H, C(3)OH)
6g	1.23 (s, 9 H, Bu^t(5)); 1.37 (s, 9 H, Bu^t(7)); 2.52 (s, 3 H, Me(7′)); 2.63 (s, 3 H, Me(8′)); 6.64 (d, 1 H, H(4), *J* = 1.86); 6.68 (d, 1 H, H(6), *J* = 1.86); 7.37 (d, 1 H, H(6′); *J* = 8.5); 7.89 (d, 1 H, H(5′), *J* = 8.5); 8.20 (s, 1 H, H(3′)); 19.31 (s, 1 H, C(3)OH)
6h	1.26 (s, 9 H, Bu^t(5)); 1.41 (s, 9 H, Bu^t(7)); 3.97 (s, 3 H, OMe(6′)); 6.65 (d, 1 H, H(4), *J* = 1.8); 6.80 (d, 1 H, H(6), *J* = 1.8); 7.38 (d, 1 H, H(7′), *J* = 9.0); 7.41 (d, 1 H, H(5′), *J* = 2.6); 7.78 (d, 1 H, H(8′), *J* = 9.0); 8.22 (s, 1 H, H(3′)); 18.53 (s, 1 H, C(3)OH)
6i	1.23 (s, 9 H, Bu^t(5)); 1.37 (s, 9 H, Bu^t(7)); 2.73 (s, 3 H, Me(8′)); 6.68 (d, 1 H, H(4), *J* = 1.82); 6.83 (d, 1 H, H(6), *J* = 1.82); 7.57—7.64 (m, 2 H, H(6′), H(7′)); 8.32 (s, 1 H, H(3′)); 18.02 (s, 1 H, C(3)OH)
6j	1.25 (s, 9 H, Bu^t(5)); 1.38 (s, 9 H, Bu^t(5)); 2.40 (s, 3 H, Me(6′)); 2.70 (s, 3 H, Me(8′)); 6.68 (d, 1 H, H(4), *J* = 1.82); 6.82 (d, 1 H, H(6), *J* = 1.82); 7.50 (s, 1 H, H(7′)); 8.28 (s, 1 H, H(3′)); 18.02 (s, 1 H, C(3)OH)
6k	1.24 (s, 9 H, Bu^t(5)); 1.39 (s, 9 H, Bu^t(7)); 2.54 (s, 3 H, Me(7′)); 2.65 (s, 3 H, Me(8′)); 6.67 (d, 1 H, H(4), *J* = 1.87); 6.81 (d, 1 H, H(6), *J* = 1.87); 7.51 (s, 1 H, H(6′)); 8.25 (s, 1 H, H(3′)); 18.30 (s, 1 H, C(3)OH)
7a	1.23 (s, 9 H, Bu^t(5)); 1.38 (s, 9 H, Bu^t(7)); 2.74 (s, 3 H, Me(8′)); 3.29 (t, 4 H, C(4′)N(CH$_2$)$_2$); 3.99 (t, 4 H, C(4′)(CH$_2$)$_2$O); 6.62 (s, 2 H, H(4), H(6)); 7.35 (t, 1 H, H(6′), *J* = 7.8); 7.5 (d, 1 H, H(7′), *J* = 7.7); 7.73 (s, 1 H, H(3′)); 7.78 (d, 1 H, H(5′), *J* = 7.7); 19.15 (br.s, 1 H, C(3)OH)
7b	1.23 (s, 9 H, Bu^t(5)); 1.38 (s, 9 H, Bu^t(7)); 2.47 (s, 3 H, Me(6′)); 2.67 (s, 3 H, Me(8′)); 3.25 (t, 4 H, morpholine); 3.98 (t, 4 H, morpholine); 6.62 (s, 2 H, H(4,6)); 7.37 (s, 1 H, H(7′)); 7.52 (s, 1 H, H(5′)); 7.65 (s, 1 H, H(3′)); 19.09 (br.s, 1 H, C(3)OH)
7c	1.24 (s, 9 H, Bu^t(5)); 1.37 (s, 9 H, Bu^t(7)); 2.50 (s, 3 H, Me(7′)); 2.62 (s, 3 H, Me(8′)); 3.28 (t, 4 H, morpholine); 3.98 (t, 4 H, morpholine); 6.61 (s, 2 H, H(4), H(6)); 7.24 (d, 1 H, H(6′), *J* = 10.33); 7.65 (d, 1 H, H(5′), *J* = 10.33); 7.66 (s, 1 H, H(3′)); 18.93 (br.s, 1 H, C(3)OH)
7d	1.24 (s, 9 H, Bu^t(5)); 1.39 (s, 9 H, Bu^t(7)); 3.25 (t, 4 H, morpholine); 3.98 (t, 4 H, morpholine), 3.97 (s, 3 H, C(6′)OMe); 6.59 (d, 1 H, H(4), *J* = 1.8); 6.69 (d, 1 H, H(6), *J* = 1.8); 7.23 (d, 1 H, H(5′), ^1J = 2.7); 7.30 (dd, 1 H, H(7′), ^1J = 2.7, ^2J = 9.0); 7.70 (d, 1 H, H(8′), *J* = 9.0); 7.70 (s, 1 H, H(3′)); 19.11 (br.s, 1 H, C(3)OH)
7e	1.28 (s, 9 H, Bu^t(5)); 1.42 (s, 9 H, Bu^t(7)); 3.32 (t, 4 H, morpholine); 4.02 (t, 4 H, morpholine); 6.72 (s, 1 H, H(4)); 6.73 (s, 1 H, H(6)); 7.70—8.00 (m, 6 H, arom.); 8.75 (d, 1 H, H(3′), *J* = 8.0); 20.05 (s, 1 H, C(3)OH)
7f	1.24 (s, 9 H, Bu^t(5)); 1.39 (s, 9 H, Bu^t(7)); 2.78 (s, 3 H, Me(8′)); 2.80—3.20 (m, 4 H, morpholine); 3.70—3.97 (m, 4 H, morpholine); 6.70 (d, 1 H, H(4), *J* = 1.8); 6.78 (d, 1 H, H(6), *J* = 1.8); 7.50—7.60 (m, 2 H, H(6′), H(7′)); 7.92 (s, 1 H, H(3′)); 18.9 (br.s, 1 H, C(3)OH)
7g	1.27 (s, 9 H, Bu^t(5)); 1.43 (s, 9 H, Bu^t(7)); 2.42 (s, 3 H, Me(6′)); 2.70 (s, 3 H, Me(8′)); 2.80—3.10 (m, 4 H, morpholine); 3.70—3.85 (m, 4 H, morpholine); 6.67 (d, 1 H, H(4), *J* = 1.70); 6.80 (d, 1 H, H(6), *J* = 1.70); 7.44 (s, 1 H, H(7′)); 7.98 (s, 1 H, H(3′)); 18.80 (s, 1 H, C(3)OH)
7h	1.26 (s, 9 H, Bu^t(5)); 1.4 (s, 9 H, Bu^t(7)); 2.54 (s, 3 H, Me(7′)); 2.65 (s, 3 H, Me(8′)); 2.82—3.22 (m, 4 H, morpholine); 3.64—3.98 (m, 4 H, morpholine); 6.66 (d, 1 H, H(4), *J* = 1.86); 6.75 (d, 1 H, H(6), *J* = 1.86); 7.46 (s, 1 H, H(6′)); 7.84 (s, 1 H, H(3′)); 19.05 (s, 1 H, C(3)OH)
7i	1.24 (s, 9 H, Bu^t(5)); 1.38 (s, 9 H, Bu^t(7)); 1.60—2.00 (m, 6 H, piperidine); 2.71 (s, 3 H, Me(8′)); 3.20—3.40 (m, 4 H, piperidine); 6.60 (s, 2 H, H(4,6)); 7.29 (t, 1 H, H(6′), *J* = 7.7); 7.45 (d, 1 H, H(7′), *J* = 7.8); 7.67 (s, 1 H, H(3′)); 7.73 (d, 1 H, H(5′), *J* = 7.8); 18.84 (br.s, 1 H, C(3)OH)
7j	1.23 (s, 9 H, Bu^t(5)); 1.37 (s, 9 H, Bu^t(7)); 1.60—2.00 (m, 6 H, piperidine); 2.47 (s, 3 H, Me(6′)); 2.67 (s, 3 H, Me(8′)); 3.2—3.4 (m, 4 H, piperidine); 6.59 (d, 1 H, H(4), *J* = 1.8); 6.60 (d, 1 H, H(6), *J* = 1.8); 7.31 (s, 1 H, H(7′)); 7.50 (s, 1 H, H(5′)); 7.66 (s, 1 H, H(3′)); 18.89 (s, 1 H, C(3)OH)
7k	1.23 (s, 9 H, Bu^t(5)); 1.37 (s, 9 H, Bu^t(7)); 1.60—2.00 (m, 6 H, piperidine); 2.49 (s, 3 H, Me(7′)); 2.61 (s, 3 H, Me(8′)); 3.20—3.40 (m, 4 H, piperidine); 6.57 (d, 1 H, H(4), *J* = 1.73); 6.60 (d, 1 H, H(6), *J* = 1.73); 7.22 (d, 1 H, H(6′), *J* = 8.53); 7.63 (d, 1 H, H(5′), *J* = 8.53); 7.63 (s, 1 H, H(3′)), 18.72 (br.s, 1 H, C(3)OH)
7l	1.25 (s, 9 H, Bu^t(5)); 1.39 (s, 9 H, Bu^t(7)); 1.60—3.20 (m, 10 H, piperidine); 2.72 (s, 3 H, Me(8′)); 6.64 (d, 1 H, H(4), *J* = 1.8); 6.72 (d, 1 H, H(6), *J* = 1.8); 7.49 (d, 1 H, H(7′), *J* = 7.7); 7.55 (d, 1 H, H(6′), *J* = 7.7); 7.85 (s, 1 H, H(3′)); 19.0 (br.s, 1 H, C(3)OH)
7m	1.25 (s, 9 H, Bu^t(5)); 1.39 (s, 9 H, Bu^t(7)); 1.60—3.20 (m, 10 H, piperidine); 2.39 (s, 3 H, Me(6′)); 2.68 (s, 3 H, Me(8′)); 6.65 (d, 1 H, H(4), *J* = 1.42); 6.74 (d, 1 H, H(6), *J* = 1.42); 7.39 (s, 1 H, H(7′)); 7.96 (s, 1 H, H(3′)); 18.96 (br.s, 1 H, C(3)OH)

(*to be continued*)

Table 2 (*continued*)

Compound	δ (*J*/Hz)
7n	1.24 (s, 9 H, Bu^t(5)); 1.38 (s, 9 H, Bu^t(7)); 1.60—3.20 (m, 10 H, piperidine); 2.51 (s, 3 H, Me(7′)); 2.62 (s, 3 H, Me(8′)); 6.62 (d, 1 H, H(4), *J* = 1.76); 6.68 (d, 1 H, H(6), *J* = 1.76); 7.47 (s, 1 H, H(6′)), 7.79 (s, 1 H, H(3′)); 19.08 (br.s, 1 H, C(3)OH)
7o	1.22 (s, 9 H, Bu^t(5)); 1.31 (s, 9 H, Bu^t(7)); 2.60 (s, 3 H, Me(8′)); 3.22 (m, 2 H, CH_2); 3.73 (m, 2 H, CH_2); 4.71 (t, 1 H, OH); 6.33 (d, 1H, H(4), *J* = 1.8); 6.43 (d, 1 H, H(6), *J* = 1.8); 7.10—7.50 (m, 4 H, arom.); 7.46 (m, 1 H, NH); 8.05 (d, 1 H, H(3′)); 18.28 (s, 1 H, C(3)OH)
7p	1.22 (s, 9 H, Bu^t(5)); 1.31 (s, 9 H, Bu^t(7)); 2.52 (s, 3 H, Me(6′)); 2.60 (s, 3 H, Me(8′)); 3.34 (m, 2 H, CH_2); 3.73 (m, 2 H, CH_2); 4.70 (t, 1 H, OH); 6.35 (d, 1 H, H(4), *J* = 1.8); 6.44 (d, 1 H, H(6), *J* = 1.8); 7.18 (s, 1 H, H(7′)); 7.24 (s, 1 H, H(5′)); 7.34 (m, 1 H, NH); 7.86 (s, 1 H, H(3′)); 18.30 (s, 1 H, C(3)OH)
7q	1.22 (s, 9 H, Bu^t(5)); 1.31 (s, 9 H, Bu^t(7)); 2.48 (s, 3 H, Me(7′)); 2.51 (s, 3 H, Me(8′)); 3.37 (m, 2 H, CH_2); 3.73 (m, 2 H, CH_2); 4.70 (t, 1 H, OH); 6.33 (d, 1 H, H(4), *J* = 1.8); 6.41 (d, 1 H, H(6), *J* = 1.8); 7.05—7.15 (m, 2 H, H(5′), H(6′)); 7.37 (m, 1 H, NH); 7.94 (d, 1 H, H(3′)); 18.16 (s, 1 H, C(3)OH)
7r	1.23 (s, 9 H, Bu^t(5)); 1.37 (s, 9 H, Bu^t(7)); 2.71 (s, 3 H, Me(8′)); 3.16 (t, 4 H, piperazine); 3.26 (t, 4 H, piperazine); 6.60 (s, 2 H, H(4,6)); 7.32 (t, 1 H, H(6′), *J* = 7.8); 7.48 (d, 1 H, H(7′), *J* = 7.8); 7.68 (s, 1 H, H(3′)); 7.76 (d, 1 H, H(5′), *J* = 7.8); 18.95 (br.s, 1 H, C(3)OH)
7s	1.23 (s, 9 H, Bu^t(5)); 1.40 (s, 9 H, Bu^t(7)); 2.48 (s, 3 H, Me(6′)); 2.67 (s, 3 H, Me(8′)); 3.17 (t, 4 H, piperazine); 3.24 (t, 4 H, piperazine); 6.61 (s, 2 H, H(4), H(6)); 7.33 (s, 1 H, H(7′)); 7.53 (s, 1 H, H(5′)); 7.68 (s, 1 H, H(3′)); 19.00 (br.s, 1 H, C(3)OH)
7t	1.23 (s, 9 H, Bu^t(5)); 1.36 (s, 9 H, Bu^t(7)); 2.50 (s, 3 H, Me(7′)); 2.61 (s, 3 H, Me(8′)); 3.15 (m, 4 H, piperazine); 3.25 (t, 4 H, piperazine); 6.58 (d, 1 H, H(4), *J* = 1.8); 6.60 (d, 1 H, H(6), *J* = 1.8); 7.23 (d, 1 H, H(6′), *J* = 8.3); 7.65 (d, 1 H, H(5′), *J* = 8.3); 7.70 (s, 1 H, H(3′)); 18.84 (s, 1 H, C(3)OH)
7u	1.22 (s, 9 H, Bu^t(5)); 1.27 (s, 9 H, Bu^t(7)); 2.72 (s, 3 H, Me(8′)); 3.89 (s, 3 H, C(5′)OMe); 3.98 (s, 3 H, C(2′)OMe); 6.57 (d, 1 H, H(4), *J* = 1.3); 6.59 (d, 1 H, H(6), *J* = 1.3); 6.68 (dd, 1 H, H(4′), J_1 = 8.9, J_2 = 2.7); 6.92 (d, 1 H, H(3′), *J* = 8.9); 7.29 (s, 1 H, C(4′)NH); 7.38 (t, 1 H, H(6′), *J* = 7.6); 7.39 (d, 1 H, H(6″), *J* = 2.7); 7.55 (d, 1 H, H(7′), *J* = 6.95); 7.75 (d, 1 H, H(5′), *J* = 8.32); 7.97 (s, 1 H, H(3′)); 18.80 (br.s, 1 H, C(3)OH)
7v	1.16 (s, 9 H, Bu^t(5)); 1.22 (s, 9 H, Bu^t(7)); 2.38 (s, 3 H, Me(4″)); 2.56 (s, 3 H, Me(7′)); 2.67 (s, 3 H, Me(8′)); 6.59 (d, 1 H, H(4), *J* = 1.3); 6.62 (d, 1 H, H(6), *J* = 1.3); 6.89 (s, 1 H, C(4′)NH); 7.05 (d, 2 H, H(3″), H(5″), *J* = 8.3); 7.21 (d, 2 H, H(2″), H(6″), *J* = 8.3); 7.55 (s, 1 H, H(6′)); 7.61 (s, 1 H, H(3′)); 18.98 (s, 1 H, OH(3))
7w	1.29 (s, 9 H, Bu^t(5)); 1.37 (s, 9 H, Bu^t(7)); 2.42 (s, 3 H, Me(6′)); 2.80 (s, 3 H, Me(8′)); 6.77 (d, 1 H, H(4), *J* = 1.7); 6.88 (d, 1 H, H(6), *J* = 1.7); 7.08 (s, 1 H, H(7′)); 7.25 (d, 1 H, H(4″), *J* = 8.55); 7.57 (d, 1 H, H(5″), *J* = 8.55); 7.59 (s, 1 H, H(3′)); 8.12 (s, 1 H, H(2″)); 17.85 (s, 1 H, C(3)OH)
7x	1.27 (s, 9 H, Bu^t(5)); 1.38 (s, 9 H, Bu^t(7)); 2.78 (s, 3 H, Me(8′)); 6.71 (d, 1 H, H(4), *J* = 1.7); 6.78 (d, 1 H, H(6), *J* = 1.7); 7.34 (s, 2 H, H(4″), H(5″)); 7.45 (t, 1 H, H(6′)); 7.62 (d, 1 H, H(7′), *J* = 8.4); 7.65 (d, 1 H, H(5′), *J* = 8.4); 7.85 (s, 1 H, H(3′)); 8.14 (s, 1 H, H(2″)); 19.01 (s, 1 H, C(3)OH)
7y	1.27 (s, 9 H, Bu^t(5)); 1.37 (s, 9 H, Bu^t(7)); 2.46 (s, 3 H, Me(6′)); 2.75 (s, 3 H, Me(8′)); 6.71 (d, 1 H, H(4), *J* = 1.7); 6.79 (d, 1 H, H(6), *J* = 1.7); 7.33 (s, 1 H, H(7′)); 7.35 (s, 1 H, H(4″)); 7.36 (s, 1 H, H(5″)); 7.49 (s, 1 H, H(5′)); 7.84 (s, 1 H, H(3′)); 8.11 (s, 1 H, H(2″)); 19.10 (s, 1 H, C(3)OH)
7z	1.27 (s, 9 H, Bu^t(5)); 1.37 (s, 9 H, Bu^t(7)); 2.56 (s, 3 H, Me(7′)); 2.69 (s, 3 H, Me(8′)); 6.70 (d, 1 H, H(4), *J* = 1.7); 6.75 (d, 1 H, H(6), *J* = 1.7); 7.32 (s, 1 H, H(4″)); 7.33 (s, 1 H, H(5″)); 7.36 (d, 1 H, H(6′), *J* = 8.5); 7.51 (d, 1 H, H(5′), *J* = 8.5); 7.84 (s, 1 H, H(3′)); 8.08 (s, 1 H, H(2″)); 19.25 (s, 1 H, C(3)OH)

that the downfield shifts of protons involved in hydrogen bonds linearly correlate with the strength of this bond. Therefore, intramolecular O—H...N and O...H—N hydrogen bonds in the conjugated chelate six-membered rings in the 2-(quinolin-2-yl)-β-tropolone molecules (**6** and **7**) are among the strongest bonds, the so-called resonance assisted hydrogen bonds (RAHB).[14,16] The six-membered ring formed with the involvement of the intramolecular hydrogen bond, the quinoline fragment, and the C(1)—C(4) atoms of the tropolone ring are in a single plane (the C(4) atom slightly deviates from this plane), whereas the seven-membered tropolone ring is bent along the C(1)—C(4) line (see Figs 1 and 2). In both compounds (**6e** and **7a**), the dihedral angles between the C(1)C(2)C(3)C(4) and C(4)C(5)C(6)C(7) planes are 37.9°.

Quantum chemical calculations by the density functional theory (DFT) method at the B3LYP/6-31G** level well reproduce the experimental geometry of molecules **6e** and **7a**, such as the shortened O...N distances and the puckering of the seven-membered ring along the C(1)—C(4) line (Fig. 3, Table 6). The differences between the calculated and experimental bond lengths are, on the average, no larger than 0.01 Å. In the crystals

(X-ray diffraction data) and the gas phase (DFT calculations), 2-(quinolin-2-yl)-β-tropolone (**6e**) containing the electron-withdrawing substituent (R^1 = Cl) at position 4

Table 3. IR spectroscopic data for 5,7-di(*tert*-butyl)-3-hydroxy-2-(quinolin-2-yl)tropones **6** and **7**

Compound	ν/cm^{-1}
6a	1633, 1607, 1593, 1553, 1447, 1367, 1300
6c	1620, 1513, 1500, 1460, 1447, 1367, 1353, 1327, 1300, 1233
6e	1660, 1647, 1607, 1580, 1513, 1473, 1420
6f	1606, 1580, 1460, 1313, 1300, 1233
6g	1633, 1607, 1580, 1500, 1447, 1367, 1220
6j	1647, 1620, 1567, 1527, 1460
6k	1647, 1607, 1580, 1527, 1460
7a	1633, 1620, 1593, 1513, 1500, 1460, 1447, 1415, 1380, 1367
7b	1633, 1607, 1580, 1460, 1447, 1367, 1273
7h	1633, 1620, 1593, 1527, 1460, 1447, 1367, 1353
7o	3420, 3260, 1633, 1607, 1580, 1513, 1447, 1393, 1367, 1353, 1340
7p	3340, 3180, 1633, 1593, 1540, 1460, 1367, 1260, 1233
7r	3328, 1593, 1580, 1553, 1500, 1460, 1407, 1367, 1313, 1273, 1233
7t	3353, 1607, 1593, 1553, 1513, 1460, 1407, 1367, 1273, 1233
7v	3380, 1633, 1580, 1500, 1433, 1367, 1353, 1233
7w	1620, 1593, 1580, 1513, 1447, 1367, 1353, 1300
7x	1633, 1607, 1500, 1460, 1407, 1367 1340, 1300, 1260, 1233

Table 4. Mass-spectrometric data (EI, 70 eV) for 5,7-di(*tert*-butyl)-3-hydroxy-2-(quinolin-2-yl)tropones **6** and **7**

Compound	*m/z* (I_{rel} (%))
6a	361 (4) $[M]^+$, 333 (62), 318 (100), 290 (29), 57 (23), 40 (80)
6d	445 (7) $[M]^+$, 417 (53), 402 (70), 190 (40), 91 (30), 57 (85), 41 (100)
6e	409 (10) $[M]^+$, 381 (90), 366 (100), 350 (40), 338 (40), 310 (45), 57 (40), 41 (50)
6f	423 (8) $[M]^+$, 395 (88), 380 (100), 352 (25), 57 (50), 41 (45)
6g	423 (2) $[M]^+$, 395 (88), 380 (100), 352 (28), 338 (12.5), 57 (35), 41 (37.5)
6i	454 (7) $[M]^+$, 426 (92), 411 (100), 383 (28), 365 (38), 57 (46), 41 (48)
6j	468 (5) $[M]^+$, 440 (75), 425 (75), 397 (20), 379 (18), 91 (33), 57 (90), 41 (100)
6k	468 (5) $[M]^+$, 440 (75), 425 (75), 397 (20), 379 (18), 91 (33), 57 (90), 41 (100)
7a	460 (8) $[M]^+$, 432 (100), 417 (75), 401 (15), 375 (18), 115 (15), 91 (18), 57 (48), 41 (52)
7b	474 (8) $[M]^+$, 446 (100), 431 (65), 415 (10), 403 (18), 45 (18)
7f	505 (8) $[M]^+$, 477 (100), 462 (44), 83 (18), 57 (10), 41 (10)
7h	519 (8) $[M]^+$, 491 (100), 476 (50), 448 (19), 57 (48), 41 (50)
7k	472 (8) $[M]^+$, 444 (100), 429 (70), 413 (14), 387 (20), 57 (52), 41 (75)
7l	503 (8) $[M]^+$, 475 (100), 460 (44), 432 (15), 45 (15)
7n	517 (8) $[M]^+$, 489 (100), 474 (44), 446 (20), 57 (68), 41 (80)
7w	500 (8) $[M]^+$, 472 (100), 457 (72), 429 (20), 91 (25), 57 (72), 41 (90)

Table 5. Selected bond lengths (*d*) and bond angles (ω) for (2-quinolin-2-yl)-β-tropolones **6e** and **7a**

Bond	*d*/Å	Bond	*d*/Å	Angle	ω/deg
		Compound **6e**			
O(1)—C(1)	1.225(2)	C(2)—C(8)	1.462(3)	C(3)—O(2)—H(2)	103.8(13)
O(2)—C(3)	1.317(3)	C(3)—C(4)	1.453(3)	C(8)—N—H(2)	101.5(9)
O(2)—H(2)	1.040(3)	C(4)—C(5)	1.350(3)	O(1)—C(1)—C(2)	127.2(2)
N—C(8)	1.340(3)	C(5)—C(6)	1.451(3)	C(3)—C(2)—C(1)	120.7(2)
C(1)—C(2)	1.476(3)	C(6)—C(7)	1.342(3)	C(3)—C(2)—C(8)	119.4(2)
C(1)—C(7)	1.476(3)	C(8)—C(9)	1.423(3)	O(2)—C(3)—C(2)	122.0(2)
C(2)—C(3)	1.400(3)			N—C(8)—C(2)	117.5(2)
		Compound **7a**			
O(1)—C(1)	1.233(4)	C(2)—C(8)	1.468(4)	C(3)—O(2)—H(1)	100(2)
O(2)—C(3)	1.305(4)	C(3)—C(4)	1.470(4)	C(8)—N(1)—H(1)	108(2)
N(1)—H(1)	0.99(4)	C(4)—C(5)	1.333(4)	O(1)—C(1)—C(2)	122.9(3)
N(1)—C(8)	1.341(4)	C(5)—C(6)	1.441(5)	C(3)—C(2)—C(1)	121.9(3)
C(1)—C(2)	1.465(5)	C(6)—C(7)	1.333(4)	C(3)—C(2)—C(8)	120.3(3)
C(1)—C(7)	1.504(4)	C(8)—C(9)	1.401(4)	O(2)—C(3)—C(2)	122.3(3)
C(2)—C(3)	1.376(4)			N—C(8)—C(2)	115.9(3)

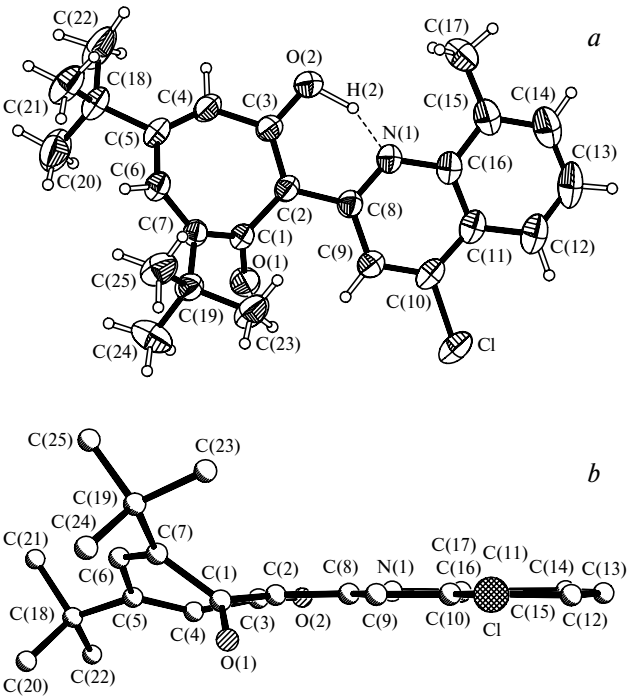


Fig. 1. Two stereo projections of the molecular structure of 5,7-di(*tert*-butyl)-2-(4-chloro-8-methylquinolin-2-yl)-3-hydroxytropone (**6e**) established by X-ray diffraction. Displacement ellipsoids are drawn at the 50% probability level. The O(2)...N(1) distance is 2.455 Å.

Table 6. Interplanar angles and the total (E_{tot}) and relative (ΔE) energies of tautomers of (2-quinolin-2-yl)-β-tropolones **6e** and **7a**

Compound	ψ/deg	E_{tot}/au	ΔE/kcal mol^{-1}
6e (OH)	32.2	−1634.973603	0
6e (NH)	33.8	−1634.972014	1.0
7a (OH)	32.1	−1461.986964	0
7a (NH)	33.6	−1461.987154	−0.12

of the quinoline ring exists as the hydroxyvinylimine (OH) tautomer. On the contrary, the aminoenone (NH) form is

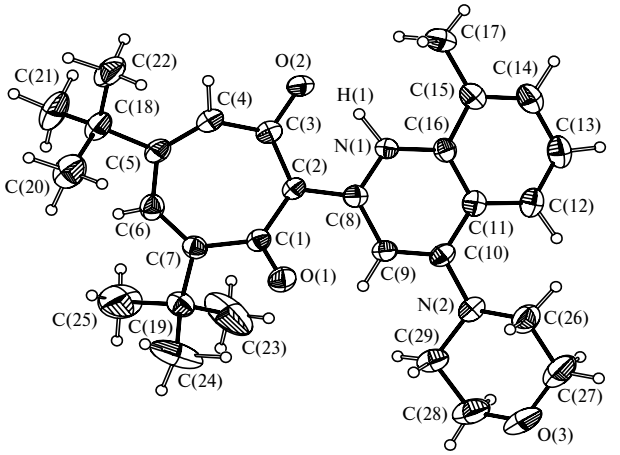


Fig. 2. Molecular structure of 5,7-di(*tert*-butyl)-3-hydroxy-2-(8-methyl-4-morpholinoquinolin-2-yl)tropone (**7a**). Displacement ellipsoids are drawn at the 50% probability level. The O(2)...N(1) distance is 2.446 Å.

favorable for 2-(quinolin-2-yl)-β-tropolone (**7a**) containing the electron-donating substituent $R^1 = NR'R''$.

The nucleophilic substitution of the chlorine atom in 2-(quinolin-2-yl)-β-tropolones **6** (R^1 = Cl) occurs in nearly quantitative yields on heating of a mixture of **6** with aliphatic, aromatic, or heterocyclic amines at 120—130 °C for 1—3 h (method ***D***, see Table 1).

Reaction mechanism. The multistep mechanism of the reaction giving rise to 2-(quinolin-2-yl)-β-tropolones **6** and **7** is presented in Scheme 2. In the initial step, aldol condensation of 2-methylquinolines **4** with 3,5-di(*tert*-butyl)-1,2-benzoquinone (**3**) affords intermediate adducts **8**. Some of these intermediates were preparatively isolated, and their structures were established by ^{1}H and ^{13}C NMR spectroscopy and mass spectrometry. The molecular structure of 2,4-di(*tert*-butyl)-6-(4-chloro-7,8-dimethylquinolin-2-ylmethylene)-6-hydroxy-2,4-cyclohexadien-1-one (**8**, R^1 = Cl, $R^2 = R^3$ = H, $R^4 = R^5$ = Me) was established by X-ray diffraction (Fig. 4, Table 7).

Intermediates **8** undergo cyclization to form norcaradiene derivatives **9**, which are rearranged into dihydrotropolones **10**. Oxidation of dihydrotropolones **10** with an

Table 7. Experimental (X-ray diffraction) and calculated (B3LYP/6-31G**) bond lengths (*d*) and bond angles (ω) for compound **8**

Bond	*d*/Å		Bond	*d*/Å		Angle	ω/deg	
	Experiment	Calculations		Experiment	Calculations		Experiment	Calculations
O(1)—C(1)	1.207	1.231	C(1)—C(2)	1.449	1.474	C(6)—C(7)—C(8)	113.7	114.3
O(2)—C(6)	1.402	1.417	C(2)—C(3)	1.365	1.361	C(1)—C(6)—C(7)	102.8	104.5
C(6)—C(7)	1.579	1.580	C(3)—C(4)	1.463	1.469	C(5)—C(6)—C(7)	111.4	109.2
C(7)—C(8)	1.511	1.511	C(4)—C(5)	1.356	1.346	N—C(8)—C(7)	117.4	116.9
C(8)—N	1.294	1.320	C(6)—C(5)	1.451	1.498	C(8)—N—C(15)	118.2	119.5
N—C(15)	1.392	1.365	C(1)—C(6)	1.552	1.539	O(1)—C(1)—C(6)	117.5	116.6
C(8)—C(9)	1.424	1.422	C(10)—Cl	1.731	1.758	O(2)—C(6)—C(5)	109.6	110.3

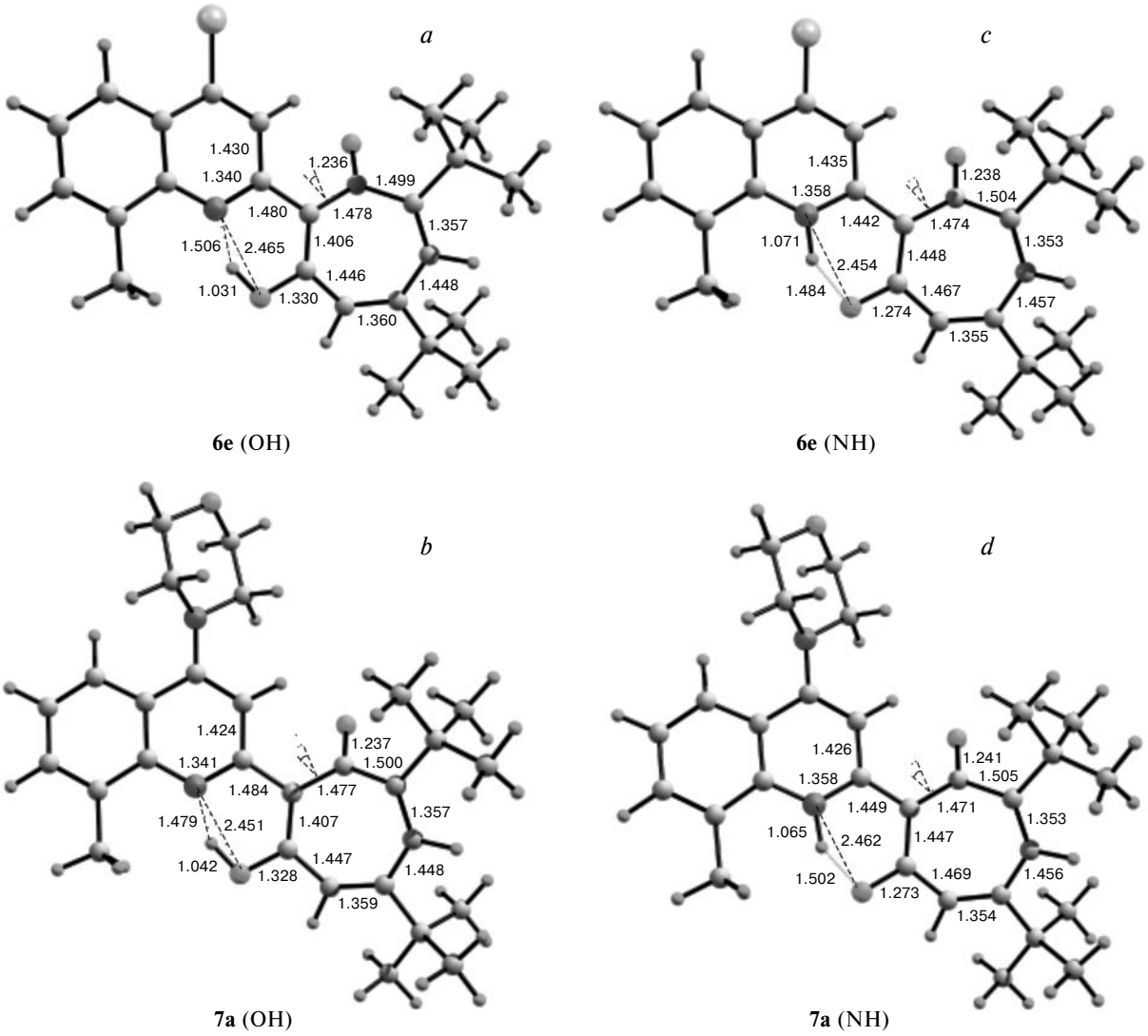


Fig. 3. Molecular geometry of the hydroxyvinylimine (*a*, *b*) and aminoenone (*c*, *d*) tautomers of 2-(quinolin-2-yl)-β-tropolones **6e** (*a*, *c*) and **7a** (*b*, *d*), calculated by the B3LYP/6-31G** method. The bond lengths are given in Å; the C(1)C(2)C(3)C(4)—C(4)C(5)C(6)C(7) interplanar angles (ψ) are listed in Table 6.

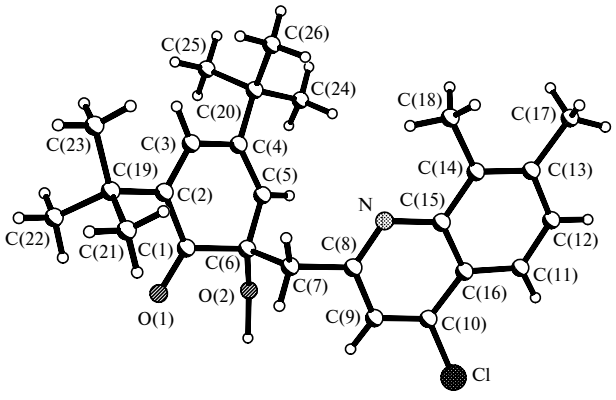
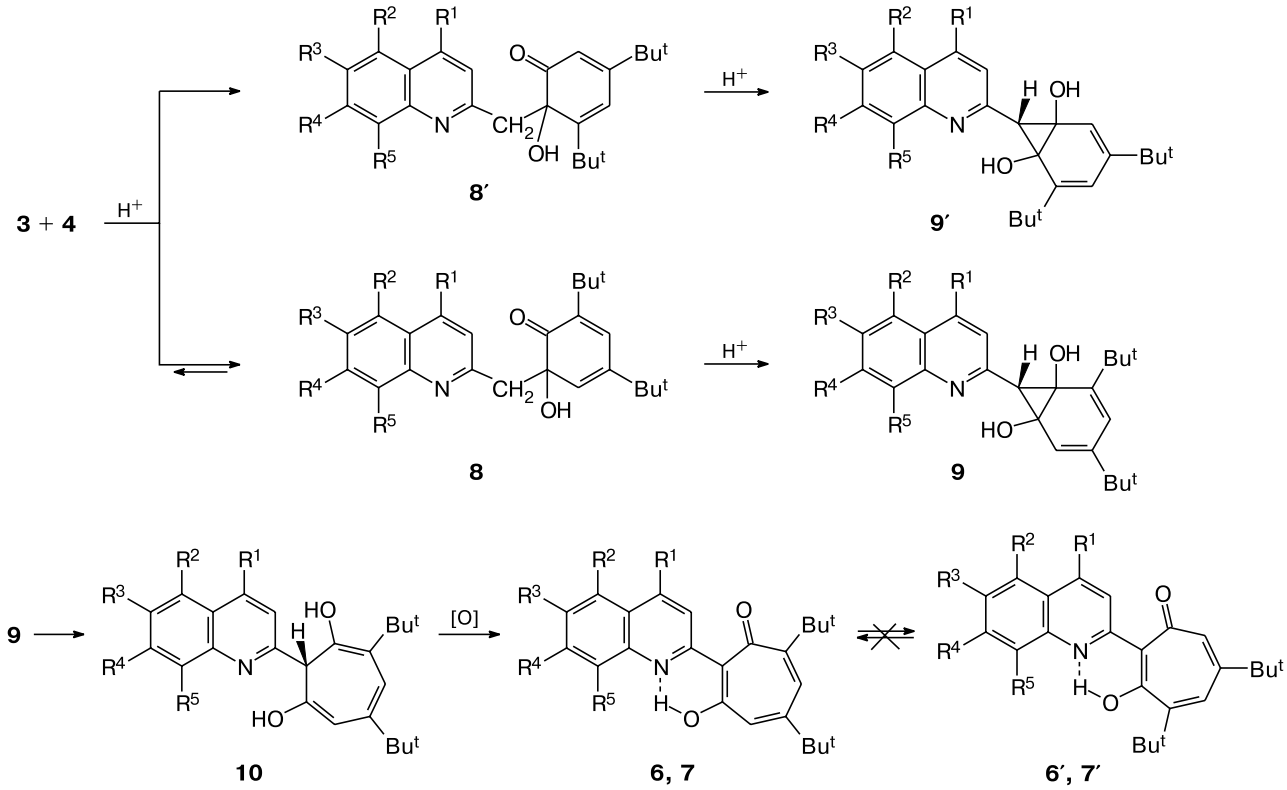


Fig. 4. Molecular structure of 2,4-di(*tert*-butyl)-6-[(4-chloroquinolin-2-yl)-7,8-dimethylmethylene]-6-hydroxy-2,4-cyclohexadien-1-one (**8**) (R^1 = Cl, R^2 = R^3 = H, R^4 = R^5 = Me).

excess of 3,5-di(*tert*-butyl)-1,2-benzoquinone (**3**) affords 5,7-di(*tert*-butyl)-2-(quinolin-2-yl)-β-tropolones **6** and **7** as the final products. In an acetic acid solution, intermediate adducts **8** are in equilibrium with the starting compounds. The involvement of these adducts in the reaction mechanism is confirmed by the fact that storage of solutions of preisolated compounds **8** in air at room temperature for 10—12 days or heating of these solutions at 40—50 °C for 20 h leads to their transformation into 2-(quinolin-2-yl)-β-tropolones **6** and **7** in 60—80% yields. The role of excess quinone **3** as an oxidizing agent is confirmed by the fact that tosyl ether of the corresponding pyrocatechol was isolated from the reaction mixture.[17]

Condensation of 2-methylquinolines **4** at another carbonyl group of quinone **3** is sterically hindered by the presence of the *tert*-butyl group adjacent to this carbonyl,

Scheme 2

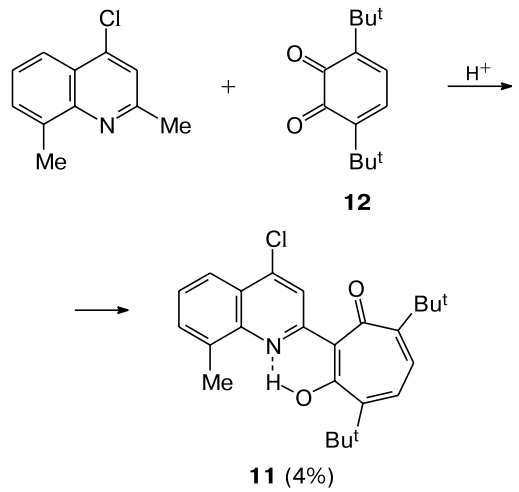


which prevents the formation of isomeric adduct **8′** and blocks the alternative reaction channel giving rise to isomeric 4,6-di(*tert*-butyl)-2-(quinolin-2-yl)-β-tropolones **6′** and **7′**. The steric hindrances caused by the *tert*-butyl group adjacent to the carbonyl group of quinone are responsible for very low (lower than 4%) yields of 2-(quinolin-2-yl)-β-tropolones **11** in condensation of 2-methylquinolines with symmetrical 3,6-di(*tert*-butyl)-1,2-benzoquinone (**12**) (Scheme 3).

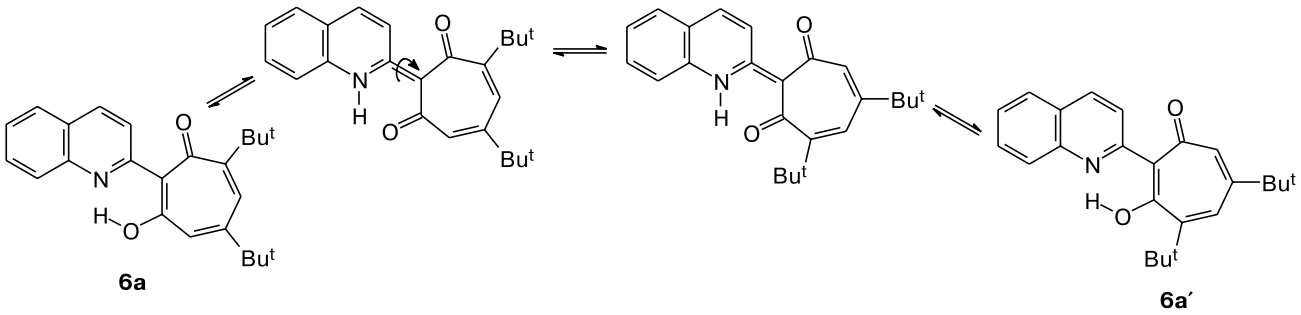
The formation of isomers **6′** and **7′** by isomerization **6**→**6′** or **7**→**7′**, which occurs by a mechanism presented in Scheme 4, is also highly unlikely because of the high energy barrier (27.6 kcal mol^{-1}, including 26.6 kcal mol^{-1} in the step of rotation about the C_{quin}—C_{trop} bond, according to B3LYP/6-31G** calculations). Calculations by the B3LYP/6-31G** method demonstrated that β-tropolones **6e** and **7a** are 2—4 kcal mol^{-1} energetically more favorable than their positional isomers **6′** and **7′**. Therefore, the formation of 2-(quinolin-2-yl)-β-tropolones **6** and **7** (see Scheme 2) is thermodynamically and kinetically controlled.

The detailed mechanism of formation of 2-(quinolin-2-yl)-β-tropolones **6** and **7** was studied by simulation of the critical regions of the potential energy surfaces (PES) for individual steps of the transformation described by Scheme 2. It was found that the preliminary proton transfer from the methylene group of intermediate adduct **8** to the nitrogen atom of the heterocycle is a necessary condition for the closure of the norcaradiene ring (**8**→**9**). Since the geometry of the H_2C—C=N triad in adduct **8** is sterically unfavorable for the intramolecular proton transfer, this reaction, like some other reactions involving the 1,3-proton transfer,[18—20] proceeds in a complex with an

Scheme 3



Scheme 4



appropriate carrier molecule, which provides a rather low barrier to the concerted double proton transfer. In the transformation under consideration, the solvent molecule (acetic acid) or the catalyst molecule (*p*-toluenesulfonic acid) serves as the proton carrier. The calculated pathway of the model reaction of *o*-benzoquinone with 4-methylquinoline, starting from the formation of a stable 1 : 1 adduct of intermediate **8** with an acetic acid molecule, is shown in Fig. 5. The structures of the intermediates and transitions states are presented in Figs 6 and 7, respectively. The corresponding energies are given in Table 8.

The proton transfer CH→N leading to the isomerization **M8**·AcOH → **M13**·AcOH is the rate-determining step of the transformation. The energy barrier for the concerted double proton transfer calculated by the B3LYP/6-31G** method is 25.4 kcal mol^{-1}. In the next step of the transformation, the solvated intermediate **M13**·AcOH is rearranged into the conformer **M´13**·AcOH, which undergoes further isomerization to form the zwitterionic intermediate **M13**$^+$·AcO$^-$ characterized by the energy barrier of 10.9 kcal mol^{-1}. The calculations demonstrated that the transformation of the zwitterion **M13**$^+$·AcO$^-$ into 1,6-dihydroxynorcaradiene can occur through two different pathways. One of these pathways is associated with the transfer of the proton of the N—H...O=C fragment (see Fig. 5, dashed line), whereas another pathway corresponds to the concerted double proton transfer through the transition state **TS4(2)** (see Fig. 7). The first pathway gives rise to the conformer of solvated 1,6-dihydroxynorcaradiene **M´9**·AcOH, whereas the second pathway (which is 5.3 kcal mol^{-1} energetically more favorable) produces the conformer **M9**·AcOH and is, consequently, the main minimum-energy reaction path to dihydro-β-tropolone **10**. It should be noted that the potential energy surface of the transformation **M13´**·AcOH → **M9**·AcOH is strongly flattened, and the inclusion of the ZPE correction into the total energy leads to a change in the order of the relative energies of the structures involved in the reaction. For example, the local minimum corresponding to the intermediate **M13**$^+$·AcO$^-$ calculated with the zero-point energy

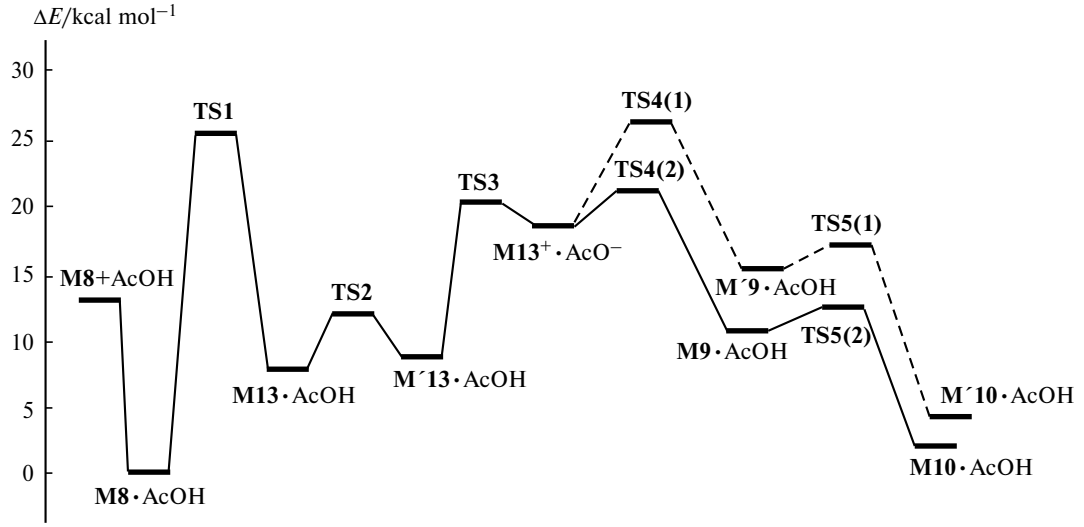


Fig. 5. Reaction energy profile of the multistep rearrangement of the solvated intermediate (**M8**) into solvated dihydro-β-tropolone (**M10**) calculated by the B3LYP/6-31G** method.

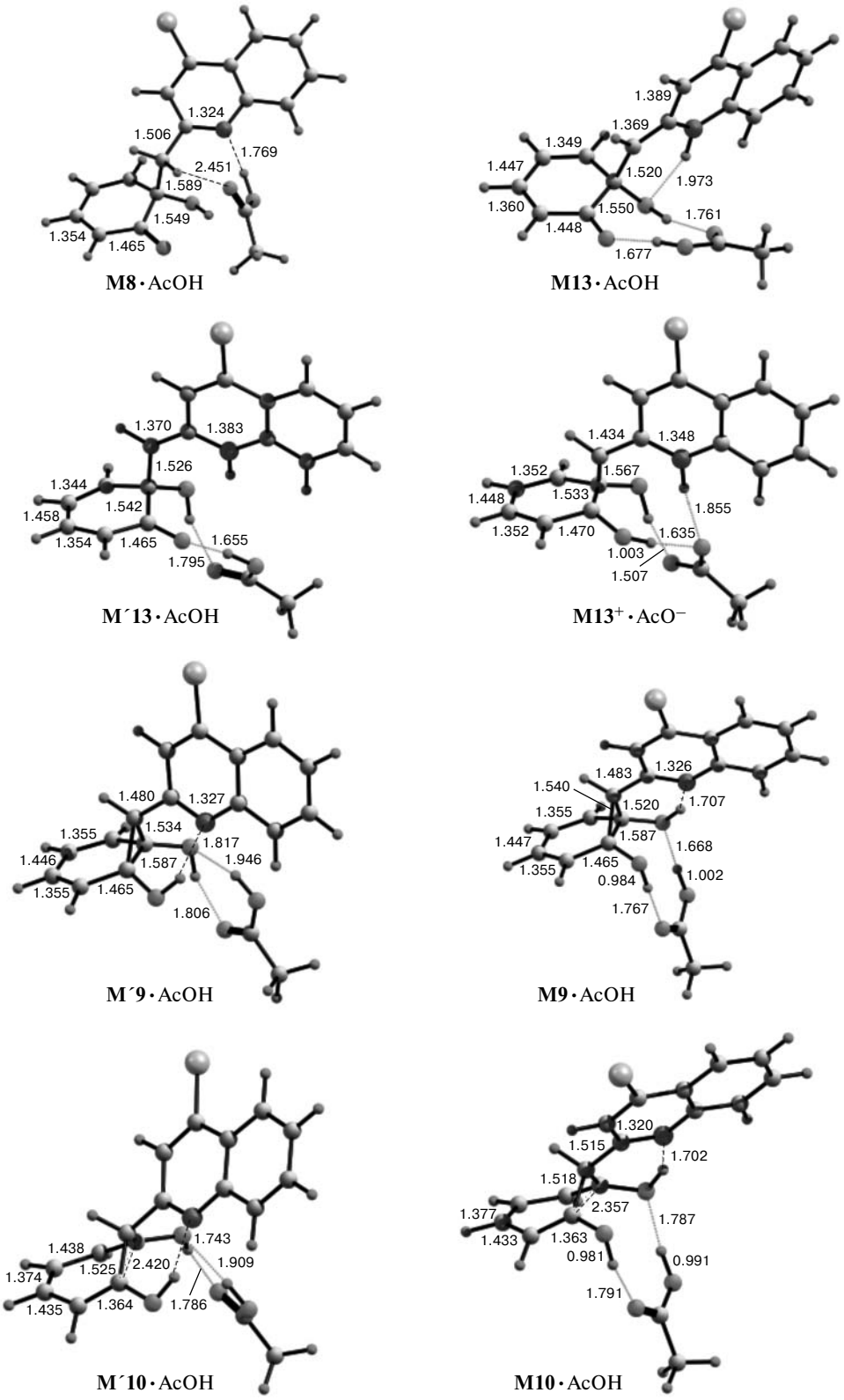


Fig. 6. The geometry of the structures (calculated by the B3LYP/6-31G** method) corresponding to the local minima shown in Fig. 5. The bond lengths are given in Å.

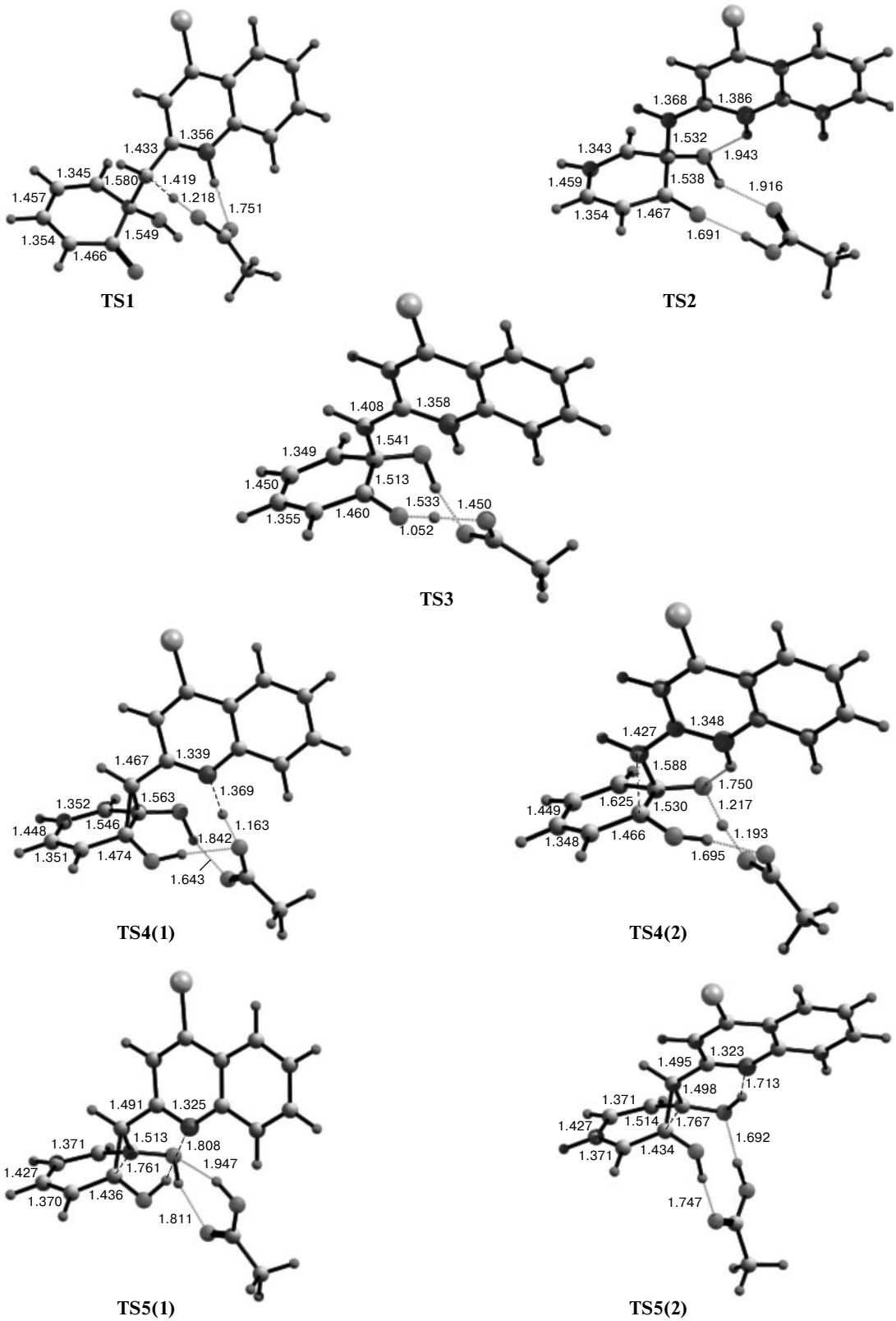


Fig. 7. The geometry of the structures (calculated by the B3LYP/6-31G** method) of the transitions states shown in Fig. 5. The bond lengths are given in Å.

Table 8. Total energies (E_{tot}), the zero point energies (ZPE), and the relative energies of the structures corresponding to the stationary points on the potential energy surface for the formation of 2-(quinolin-2-yl)-β-tropolones

Structure	$-E_{tot}$*	ZPE	ΔE /kcal mol^{-1}
	au		
M8·AcOH	1511.429465	0.306917	0
TS1	1511.388908 (*i*1192.5)	0.301741	25.4
M13·AcOH	1511.416592	0.307066	8.1
TS2	1511.410618 (*i*29.1)	0.306139	11.8
M´13·AcOH	1511.415293	0.306917	8.9
TS3	1511.397894 (*i*206.7)	0.304663	19.8
M13$^+$·AcO$^-$	1511.399071	0.306141	19.1
TS4(1)	1511.387803 (*i*817.3)	0.302192	26.1
M´9·AcOH	1511.404279	0.307171	15.8
TS5(1)	1511.402998 (*i*339.9)	0.306484	16.6
M´10·AcOH	1511.424287	0.308096	3.2
TS4(2)	1511.396311 (*i*375.6)	0.301843	20.8
M9·AcOH	1511.411150	0.306896	11.5
TS5(2)	1511.409716 (*i*335.4)	0.306220	12.4
10·AcOH	1511.425152	0.307183	2.7

* The imaginary vibrational frequencies (cm^{-1}) for the transition states are given in parentheses.

correction is higher than the energy levels of the two adjacent transitions states **TS3** and **TS4(2)**. In such cases described in the literature (see, for example, the study[21] and references therein), it is necessary to apply a more rigorous approach to studies of the corresponding regions of the potential energy surface using an anharmonic approximation. Since this detailed investigation is beyond the scope of the present study, the ZPE correction was ignored in estimating the relative energies shown in Fig. 5. The intermediates **M9**·AcOH and **M´9**·AcOH readily undergo the rearrangement (the energy barriers are as low as 0.9 and 0.8 kcal mol^{-1}, respectively) accompanied by expansion of the six-membered ring to form dihydro-β-tropolones **M10**·AcOH and **M´10**·AcOH. Subsequent oxidation of compounds **10** with quinone **3** affords 2-(quinolin-2-yl)-β-tropolones of types **6** and **7** as the final products.

We also performed B3LYP/6-31G** calculations for the rearrangement of the unsolvated intermediate **M13** with the proton transferred from the methylene group to the nitrogen atom of the quinoline ring. The results of calculations presented in Fig. 8 and Table 9 agree well with the results of calculations, in which solvation by one

Table 9. Total energies (E_{tot}), the zero point energies (ZPE), and the relative energies (with the ZPE correction) of the structures corresponding to the stationary points on the potential energy surface for the reaction shown in Fig. 8

Structure	$-E_{tot}$*	ZPE	ΔE /kcal mol^{-1}
	au		
M13	1282.297686	0.242690	8.4
TS6	1282.274865 (*i*911.9)	0.238337	20.0
M´8	1282.292376	0.243034	12.0
TS7	1282.289275 (*i*327.5)	0.241967	13.2
M´9	1282.312358	0.243966	0

* The imaginary vibrational frequencies (cm^{-1}) for the transition states are given in parentheses.

acetic acid molecule was taken into account (see Fig. 5). The calculated barrier for the reverse norcaradiene rearrangement of the 1,3,5-cycloheptatriene derivative **M´10** into **M´9** is 13.2 kcal mol^{-1}. This value is rather close to the experimental energy barrier for thermal isomerization of unsubstituted 1,3,5-cycloheptatriene into norcaradiene (11 kcal mol^{-1})[22] and the barrier for the latter reaction calculated by the B3LYP/6-31G* method (10.0 kcal mol^{-1}).[23] Therefore, it can be concluded that the reaction mechanism shown in Scheme 2 agrees well with the calculated data.

Synthesis of 5,7-di(*tert*-butyl)-4-nitro-2-(quinolin-2-yl)-β-tropolones 15 and 4,6-dioxo-2-azabicyclo[3.3.0]-octa-2,7-diene *N*-oxides 16. 5,7-Di(*tert*-butyl)-4-nitro-2-(quinolin-2-yl)-β-tropolones **15** (Table 10) and 5,7-di(*tert*-butyl)-2-(quinolin-2-yl)-β-tropolones **6** and **7** containing no nitro groups in the tropolone moiety were prepared in low yields by refluxing a solution of 2-methylquinoline **4** (R^1 = H or Cl) and 4,6-di(*tert*-butyl)-3-nitro-1,2-benzoquinone (**14**)[24] in *o*-xylene for 1 h (the conditions corresponding to the method ***B*** used for the synthesis of 2-(quinolin-2-yl)-β-tropolones **6** and **7**). Under the same conditions, the reactions of quinolines **4** (R^1 = NO_2 or morpholino) with quinone **14** produced easily isolable yellow crystals of 4,6-dioxo-2-azabicyclo[3.3.0]octa-2,7-diene *N*-oxides **16** (Scheme 5, Table 11). The structures of these crystalline products were established by X-ray diffraction. The physicochemical characteristics of compounds **15** and **16** are given in Tables 10—14. The probable reaction mechanism for the formation of bicyclic compounds **16** is presented in Scheme 6.

The molecular structures of two compounds, which are representatives of the previously unknown heterocyclic system **16**, are shown in Figs 9 and 10. Selected bond lengths and bond angles are given in Table 15. The intramolecular electrophilic addition of the nitrogen atom

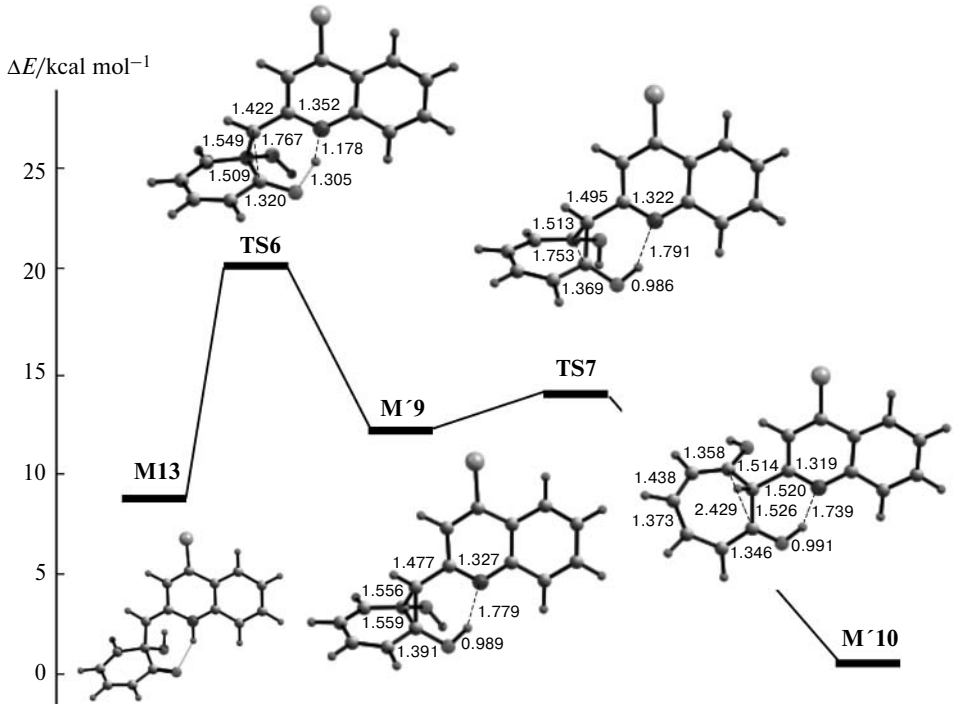


Fig. 8. Theoretical simulation of the reaction mechanism of the gas-phase rearrangement of the intermediate (**M13**) into dihydronorcaradiene (**M´9**) followed by the transformation into dihydro-β-tropolone (**M´10**). The bond lengths are given in Å.

of the nitro group to the methine carbon atom in the initially formed intermediate product **17** of aldol condensation of quinoline **4** with quinone **14** is the critical step of the transformation. Intramolecular cyclization of the product of aldol condensation of *o*-nitrobenzaldehyde with acetone, which is the rate-determining step of the classical Baeyer—Drewson indigo synthesis,[25] is the direct analog of the above reaction. The reaction producing 4,6-dioxo-2-azabicyclo[3.3.0]octa-2,7-diene *N*-oxides **16** can, presumably, further proceed as a sequence of the transformations **17** → **18** → **19** → **16**.

By-products of the reaction. The transformations presented in Schemes 1 and 5 occur under rather severe conditions and, consequently, they are accompanied by

Scheme 5

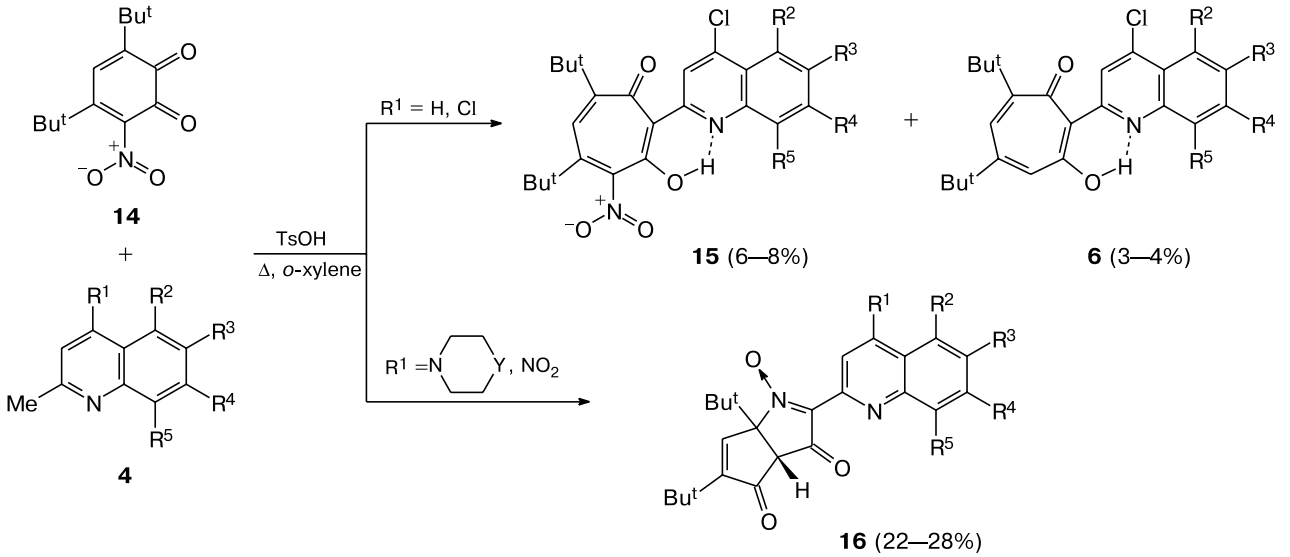
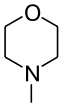
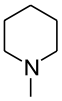


Table 10. Yields, the melting points, and elemental analysis data for 5,7-di(*tert*-butyl)-3-hydroxy-4-nitro-2-(quinolin-2-yl)tropones **15**

Compound	R^1	R^2	R^3	R^4	R^5	Yield (%) (Method)	M.p. /°C	Found / Calculated (%)				Molecular formula
								C	H	Cl	N	
15a	H	H	H	H	H	7(**B**)	233—235	70.83 70.92	6.38 6.45	—	6.79 6.89	$C_{24}H_{26}N_2O_4$
15b	Cl	H	H	7,8-Benzo		6(**B**)	259—261	68.41 68.50	5.50 5.54	7.13 7.22	5.64 5.71	$C_{28}H_{27}ClN_2O_4$
15c	Cl	H	H	H	Me	6(**B**)	228—230	66.12 66.00	5.73 5.98	7.62 7.79	6.04 6.16	$C_{25}H_{27}ClN_2O_4$
15d	Cl	H	Me	H	Me	6(**B**)	214—216	66.47 66.59	6.01 6.23	7.45 7.56	6.02 5.97	$C_{26}H_{29}ClN_2O_4$
15e	Cl	H	H	Me	Me	8(**B**)	200—202	66.48 66.59	6.15 6.23	7.49 7.56	6.01 5.97	$C_{26}H_{29}ClN_2O_4$
15f	Cl	NO_2	H	H	Me	7(**B**)	250—252	60.02 60.06	5.11 5.24	7.13 7.09	8.29 8.40	$C_{25}H_{26}ClN_3O_6$
15g	Cl	NO_2	Me	H	Me	6(**B**)	250—252	66.64 66.59	6.21 6.23	7.4 7.56	5.92 5.97	$C_{26}H_{28}ClN_3O_6$
15h	Cl	NO_2	H	Me	Me	7(**B**)	240—242	60.66 60.76	5.45 5.49	6.96 6.90	8.09 8.18	$C_{26}H_{28}ClN_3O_6$
15i		H	H	H	Me	89(**D**)	220—222	68.62 68.89	6.73 6.98	—	8.14 8.31	$C_{29}H_{35}N_3O_5$
15j		H	Me	H	Me	88(**D**)	195—197	69.22 69.34	6.93 7.18	—	8.18 8.09	$C_{30}H_{37}N_3O_5$
15k		H	H	Me	Me	91(**D**)	238—240	69.26 69.34	7.04 7.18	—	7.88 8.09	$C_{30}H_{37}N_3O_5$
15l		H	OMe	H	H	90(**D**)	200—202	66.56 66.78	6.74 6.76	—	7.98 8.06	$C_{29}H_{35}N_3O_6$
15m		H	H	H	Me	90(**D**)	199—201	71.62 71.54	7.43 7.40	—	8.12 8.34	$C_{30}H_{37}N_3O_4$
15n		H	Me	H	Me	84(**D**)	204—206	71.82 71.93	7.48 7.59	—	7.92 8.12	$C_{31}H_{39}N_3O_4$
15o		H	H	7,8-Benzo		89(**D**)	221—223	73.32 73.44	6.80 6.91	—	7.64 7.79	$C_{33}H_{37}N_3O_4$

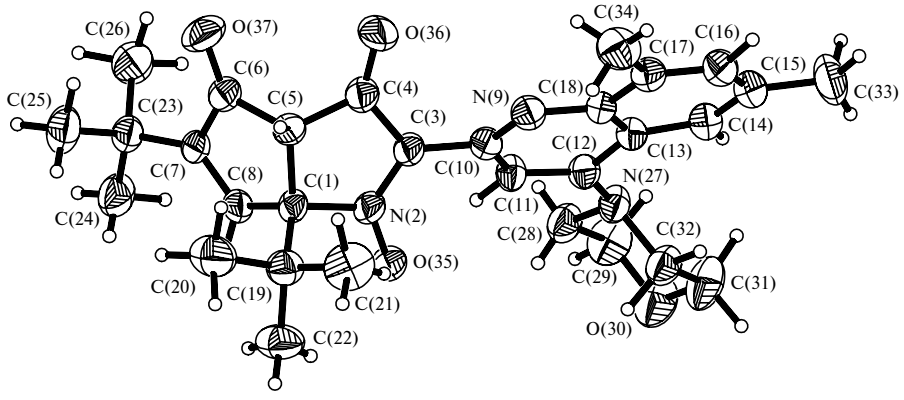


Fig. 9. Molecular structure of 1,7-di(*tert*-butyl)-3-(6,8-dimethyl-4-morpholinoquinolin-2-yl)-4.6-dioxo-2-azabicyclo[3.3.0]octa-2,7-diene *N*-oxide (**16b**). Displacement ellipsoids are drawn at the 50% probability level. The angle between the C(1)N(2)C(3)C(4)C(5) and C(1)C(8)C(7)C(6)C(5) planes is 120.4°. The C(4)C(3)C(10)C(11) dihedral angle is 140.1(2)°.

Table 11. Yields, the melting points, and elemental analysis data for 4,6-dioxo-2-azabicyclo[3.3.0]octa-2,7-diene *N*-oxides (**16**)

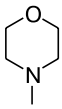
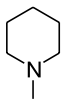
Compound	R^1	R^2	R^3	R^4	R^5	Yield (%)	M.p. /°C	Found / Calculated (%)			Molecular formula
								C	H	N	
16a		H	H	H	Me	28	210—212	71.08 71.14	7.02 7.21	8.46 8.58	$C_{29}H_{35}N_3O_4$
16b		H	Me	H	Me	26	220—222	71.48 71.54	7.36 7.40	8.18 8.34	$C_{26}H_{32}ClNO_2$
16c		H	H	Me	Me	22	237—239	71.38 71.54	7.32 7.40	8.36 8.34	$C_{30}H_{37}N_3O_4$
16d		NO_2	H	H	Me	22	219—221	67.48 67.65	6.72 6.81	10.38 10.52	$C_{30}H_{36}N_4O_5$
16e		NO_2	Me	H	Me	20	221—223	68.08 68.11	6.92 7.01	10.14 10.25	$C_{31}H_{38}N_4O_5$

Table 12. ^{1}H NMR spectroscopic data for 5,7-di(*tert*-butyl)-3-hydroxy-4-nitro-2-(quinolin-2-yl)tropones (**15**) and 4,6-dioxo-2-azabicyclo[3.3.0]octa-2,7-diene *N*-oxides (**16**)

Compound	δ (*J*/Hz)
15a	1.30 (s, 9 H, Bu^t(5)); 1.31 (s, 9 H, Bu^t(7)); 6.37 (s, 1 H, H(6)); 7.45—8.25 (m, 6 H, quinoline); 18.00 (br.s, 1 H, C(3)OH)
15b	1.33 (s, 9 H, Bu^t(5)); 1.35 (s, 9 H, Bu^t(7)); 6.47 (s, 1 H, H(6)); 7.78—8.72 (m, 6 H, arom.); 8.47 (s, 1 H, H(3′)); 19.52 (br.s, 1 H, C(3)OH)
15c	1.30 (s, 9 H, Bu^t(5)); 1.31 (s, 9 H, Bu^t(7)); 2.72 (s, 3 H, Me(8′)); 6.38 (s, 1 H, H(6)); 7.51 (t, 1 H, H(6′), *J* = 7.7); 7.65 (d, 1 H, H(7′), *J* = 7.6); 8.03 (d, 1 H, H(5′), *J* = 7.6); 8.34 (s, 1 H, H(3′)); 18.03 (br.s, 1 H, C(3)OH)
15d	1.30 (s, 9 H, Bu^t(5)); 1.31 (s, 9 H, Bu^t(7)); 2.65 (s, 3 H, Me(6′)); 2.69 (s, 3 H, Me(8′)); 6.38 (s, 1 H, H(6)); 7.48 (s, 1 H, H(7′)); 7.80 (s, 1 H, H(5′)); 8.32 (s, 1 H, H(3′)); 18.12 (br.s, 1 H, C(3)OH)
15e	1.30 (s, 9 H, Bu^t(5)); 1.31 (s, 9 H, Bu^t(7)); 2.54 (s, 3 H, Me(7′)); 2.61 (s, 3 H, Me(8′)); 6.36 (s, 1 H, H(6)); 7.43 (d, 1 H, H(6′), *J* = 8.4); 7.92 (d, 1 H, H(5′), *J* = 8.4); 8.28 (s, 1 H, H(3′)); 17.93 (br.s, 1 H, C(3)OH)
15f	1.30 (s, 9 H, Bu^t(5)); 1.31 (s, 9 H, Bu^t(7)); 2.78 (s, 3 H, Me(8′)); 6.52 (s, 1 H, H(6)); 7.58 (d, 1 H, H(7′), *J* = 8.5); 7.68 (d, 1 H, H(6′), *J* = 8.5); 8.40 (s, 1 H, H(3′)); 18.40 (br.s, 1 H, C(3)OH)
15g	1.25 (s, 9 H, Bu^t(5)); 1.38 (s, 9 H, Bu^t(5)); 2.40 (s, 3 H, Me(6′)); 2.70 (s, 3 H, Me(8′)); 6.68 (d, 1 H, H(4), *J* = 1.82); 6.82 (d, 1 H, H(6), *J* = 1.82); 7.50 (s, 1 H, H(7′)); 8.28 (s, 1 H, H(3′)); 18.02 (s, 1 H, C(3)OH)
15h	1.30 (s, 9 H, Bu^t(5)); 1.32 (s, 9 H, Bu^t(7)); 2.58 (s, 3 H, Me(7′)); 2.65 (s, 3 H, Me(8′)); 6.44 (s, 1 H, H(6)); 7.52 (s, 1 H, H(6′)); 8.32 (s, 1 H, H(3′)); 18.29 (br.s, 1 H, C(3)OH)
15i	1.30 (s, 18 H, Bu^t(5), Bu^t(7)); 2.69 (s, 3 H, Me(8′)); 3.34 (m, 4 H, morpholine); 3.99 (m, 4 H, morpholine); 6.33 (s, 1 H, H(6)); 7.38 (t, 1 H, H(6′), *J* = 7.7); 7.53 (d, 1 H, H(7′), *J* = 7.6); 7.75 (d, 1 H, H(5′), *J* = 7.6); 7.77 (s, 1 H, H(3′)); 17.15 (br.s, 1 H, C(3)OH)
15j	1.31 (s, 18 H, Bu^t(5), Bu^t(7)); 2.48 (s, 3 H, Me(6′)); 2.65 (s, 3 H, Me(8′)); 3.30 (m, 4 H, morpholine); 3.99 (m, 4 H, morpholine); 6.32 (s, 1 H, H(6)); 7.34 (s, 1 H, H(7′)); 7.51 (s, 1 H, H(5′)); 7.70 (s, 1 H, H(3′)); 17.10 (br.s, 1 H, C(3)OH)
15k	1.30 (s, 18 H, Bu^t(5), Bu^t(7)); 2.49 (s, 3 H, Me(7′)); 2.58 (s, 3 H, Me(8′)); 3.34 (m, 4 H, morpholine); 4.00 (m, 4 H, morpholine); 6.32 (s, 1 H, H(6)); 7.27 (d, 1 H, H(5′), *J* = 8.5); 7.64 (d, 1 H, H(6′), *J* = 8.5); 7.72 (s, 1 H, H(3′)); 17.06 (br.s, 1 H, C(3)OH)
15l	1.30 (s, 18 H, Bu^t(5), Bu^t(7)); 3.30 (t, 4 H, morpholine); 3.92 (s, 3 H, O(6′)Me); 4.00 (t, 4 H, morpholine); 6.37 (s, 1 H, H(6)); 7.21 (d, 1 H, H(5′), *J* = 2.7); 7.32 (d.d, 1 H, H(7′), J_1 = 9.0, J_2 = 2.7); 7.63 (d, 1 H, H(8′), *J* = 9.0); 7.77 (s, 1 H, H(3′)); 17.52 (br.s, 1 H, C(3)OH)
15m	1.29 (s, 18 H, Bu^t(5), Bu^t(7)); 1.6—2.0 (m, 6 H, piperidine); 2.67 (s, 3 H, Me(8′)); 3.2—3.4 (m, 4 H, piperidine); 6.31 (s, 1 H, H(6)); 7.32 (t, 1 H, H(6′), *J* = 7.8); 7.49 (d, 1 H, H(7′), *J* = 7.8); 7.71 (d, 1 H, H(5′), *J* = 7.8); 7.74 (s, 1 H, H(3′)); 16.94 (br.s, 1 H, C(3)OH)

(*to be continued*)

Table 12 (*continued*)

Compound	δ (*J*/Hz)
15n	1.30 (s, 18 H, Bu^t(5,7)); 1.7—1.9 (m, 6 H, piperidine); 2.47 (s, 3 H, Me(6′)); 2.64 (s, 3 H, Me(8′)); 3.2—3.5 (m, 4 H, piperidine); 6.31 (s, 1 H, H(6)); 7.33 (s, 1 H, H(7′)); 7.50 (s, 1 H, H(5′)); 7.72 (s, 1 H, H(3′)); 16.98 (br.s, 1 H, C(3)OH)
15o	1.31 (s, 18 H, Bu^t(5), Bu^t(7)); 1.7—1.9 (m, 6 H, piperidine); 3.35 (m, 4 H, piperidine); 6.37 (s, 1 H, H(6)); 7.7—8.0 (m, 6 H, arom.); 8.60 (d, 1 H, H(3′)); 18.38 (br.s, 1 H, C(3)OH)
16a	1.23 (s, 18 H, Bu^t(1), Bu^t(7)); 2.82 (s, 3 H, Me(8′)); 3.25 (t, 4 H, morpholine); 3.78 (s, 1 H, H(5)); 3.98 (t, 4 H, morpholine); 7.41 (t, 1 H, H(6′), *J* = 7.5); 7.53 (d, 1 H, H(7′), *J* = 7.5); 7.61 (s, 1 H, H(8)); 7.73 (s, 1 H, H(3′)); 7.84 (d, 1 H, H(5′), *J* = 7.5)
16b	1.23 (s, 18 H, Bu^t(1), Bu^t(7)); 2.50 (s, 3 H, Me(6′)); 2.79 (s, 3 H, Me(8′)); 3.22 (m, 4 H, C(4′)N(CH$_2$)$_2$); 3.77 (s, 1 H, H(5)); 3.99 (m, 4 H, O(CH$_2$)$_2$C(4′)); 7.37 (s, 1 H, H(7′)); 7.59 (s, 1 H, H(5′)); 7.60 (s, 1 H, H(8)); 7.75 (s, 1 H, H(3′))
16c	1.23 (s, 18 H, Bu^t(1), Bu^t(7)); 2.48 (s, 3 H, Me(7′)); 2.79 (s, 3 H, Me(8′)); 3.23 (t, 4 H, morpholine); 3.77 (s, 1 H, H(5)); 3.98 (t, 2 H, morpholine); 7.33 (d, 1 H, H(6′), *J* = 8.5); 7.61 (s, 1 H, H(8)); 7.73 (s, 1 H, H(3′)); 7.75 (d, 1 H, H(5′), *J* = 8.5)
16d	1.23 (s, 18 H, Bu^t(1,7)); 1.6—1.9 (m, 6 H, piperidine); 2.6—2.8 (m, 2 H, piperidine); 2.84 (s, 3 H, Me(8′)); 3.2—3.4 (m, 2 H, piperidine); 3.78 (s, 1 H, H(5)); 7.50 (d, 1 H, H(6′), *J* = 8.0); 7.59 (s, 1 H, H(8)); 7.64 (d, 1 H, H(7′), *J* = 8.0); 7.98 (s, 1 H, H(3′))
16e	1.23 (s, 18 H, Bu^t(1,7)); 1.71 (m, 6 H, piperidine); 2.49 (s, 3 H, Me(7′)); 2.73 (m, 2 H, piperidine); 2.80 (s, 3 H, Me(8′)); 3.30 (m, 2 H, piperidine); 3.79 (s, 1 H, H(5)); 7.50 (s, 1 H, H(6′)); 7.59 (s, 1 H, H(8)); 7.96 (s, 1 H, H(3′))

the formation of by-products of the reaction. Presently, we preparatively isolated two of these products and established their structures by X-ray diffraction. The reactions of 4-chloro-2,7,8-trimethylquinoline (**4**, R^1 = Cl, R^2 = R^3 = H, R^4 = R^5 = Me) and 3,5-di(*tert*-butyl)-1,2-benzoquinone (**3**) under the conditions described for the methods ***A*** and ***B*** produced a derivative of the new polyfused heterocyclic system, *viz.*, 8,9a,11,13-tetra(*tert*-butyl)-16-chloro-3,4-dimethylcyclopenta-[2′,3′]-chromeno[4′,3′:3,4]pyrrolo[1,2-*a*]quinoline-6,7(9a*H*)-dione (**20**), in 6% yield. The structure of molecule **20** was established by X-ray diffraction.[26] Apparently, the formation of compound **20** is preceded by acid-catalyzed dimerization of quinone **3**. However, an additional investigation is

Scheme 6

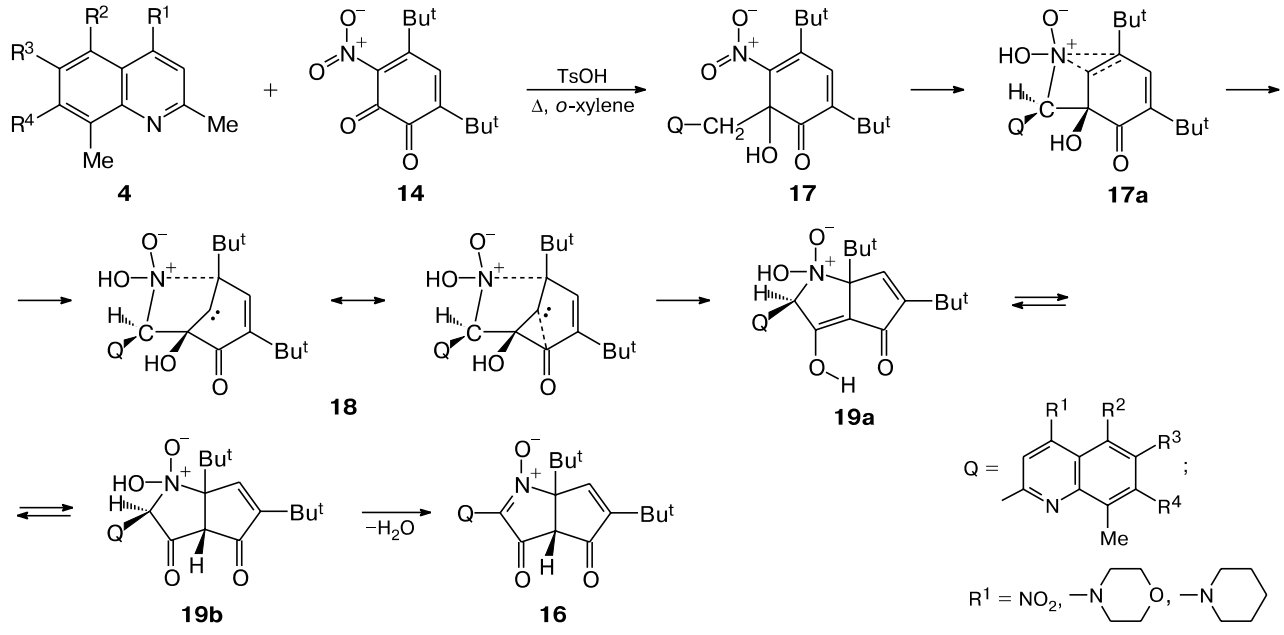


Table 13. Mass-spectrometric data (EI, 70 eV) for 5,7-di(*tert*-butyl)-3-hydroxy-4-nitro-2-(quinolin-2-yl)tropones (**15**)

Compound	*m/z* (I_{rel} (%))
15a	406 (15) $[M]^+$, 378 (40), 360 (95), 128 (100), 91 (34), 57 (65), 41 (95)
15b	490 (15) $[M]^+$, 462 (30), 444 (70), 190 (60), 91 (28), 57 (80), 41 (100)
15c	454 (10) $[M]^+$, 426 (25), 408 (50), 384 (10), 352 (25), 322 (20), 176 (30), 154 (30), 91 (35), 57 (70), 41(100)
15d	468 (15) $[M]^+$, 440 (45), 422 (100), 398 (15), 366 (15), 154 (10), 91 (15), 57 (30), 41(35)
15g	468 (5) $[M]^+$, 440 (75), 425 (75), 397 (20), 379 (18), 91 (33), 57 (90), 41 (100)
15m	1633, 1607, 1590, 1527, 1460, 1420, 1367, 1340, 1273, 1233

Table 14. IR spectroscopic data for 2-azabicyclo[3.3.0]octa-2,7-diene-4,6-dione *N*-oxides (**16**)

Compound	ν/cm^{-1}
16a	1740, 1700, 1567, 1513, 1500, 1447, 1400, 1367, 1340, 1246, 1233, 1220, 1180, 1140, 1100
16b	1740, 1700, 1620, 1580, 1527, 1460, 1367
16c	1740, 1700, 1580, 1527, 1500, 1460, 1447, 1433, 1400, 1313, 1273, 1246, 1233, 1220, 1180, 1150, 1100
16d	1740, 1700, 1580, 1527, 1500, 1460, 1447, 1400, 1313, 1273, 1246, 1233, 1220, 1180, 1150, 1100
16e	1740, 1700, 1620, 1580, 1527, 1500, 1460, 1447, 1400, 1313, 1273, 1246, 1233, 1220, 1180, 1150, 1100

required for an understanding of the detailed reaction mechanism.

The presence of considerable amounts (~10%) of 2-(2-hydroxybenzoyl)quinoline derivative **21** was particularly unexpected for us. The structure of this derivative was established by X-ray diffraction (Fig. 11, Table 16).

To elucidate the mechanism of formation of quinoline **21** as a product of the side reaction shown in Scheme 1, we performed model (alkyl groups were ignored) B3LYP/6-31G** calculations, which revealed the sequence of transformations giving rise to ketone **21** (Scheme 7, Fig. 12). The data on the energy characteristics of the structures involved in the reaction are given in Table 17. Dehydration of the initially formed adduct **8** affords stable methylenequinone hydrate **5**, which is transformed into carbinol **22** with a low energy barrier

Table 15. Selected bond lengths (*d*) and bond angles (ω) for compounds **16b** and **16d**

Bond	*d*/Å	Angle	ω/deg	Angle	ω/deg
		Compound **16b**			
C(1)—C(8)	1.512(5)	C(8)—C(1)—C(5)	104.1(3)	O(36)—C(4)—C(3)	126.6(3)
C(1)—C(5)	1.522(4)	C(8)—C(1)—N(2)	109.0(3)	O(36)—C(4)—C(5)	125.1(3)
C(1)—N(2)	1.532(4)	C(5)—C(1)—N(2)	102.1(2)	C(3)—C(4)—C(5)	108.3(3)
N(2)—O(35)	1.252(3)	N(2)—C(1)—C(19)	109.7(3)	C(10)—N(9)—C(18)	117.6(3)
N(2)—C(3)	1.322(4)	O(35)—N(2)—C(3)	126.7(3)	N(9)—C(10)—C(11)	124.5(3)
C(3)—C(4)	1.473(5)	O(35)—N(2)—C(1)	118.5(3)	N(9)—C(10)—C(3)	115.1(3)
C(3)—C(10)	1.474(5)	C(3)—N(2)—C(1)	114.7(3)	C(11)—C(10)—C(3)	120.3(3)
C(4)—O(36)	1.198(4)	N(2)—C(3)—C(4)	108.2(3)	C(4)—C(3)—C(10)	128.5(3)
C(4)—C(5)	1.516(5)	N(2)—C(3)—C(10)	123.3(3)		
C(6)—O(37)	1.204(4)				
		Compound **16d**			
C(1)—C(8)	1.503(2)	C(8)—C(1)—C(5)	103.8(1)	N(2)—C(3)—C(10)	123.1(2)
C(1)—C(5)	1.522(2)	C(8)—C(1)—N(2)	106.6(1)	C(4)—C(3)—C(10)	127.1(2)
C(1)—N(2)	1.524(2)	C(5)—C(1)—N(2)	102.7(2)	O(36)—C(4)—C(3)	126.9(2)
N(2)—O(35)	1.259(2)	C(5)—C(1)—C(19)	116.3(1)	O(36)—C(4)—C(5)	125.1(2)
N(2)—C(3)	1.324(2)	N(2)—C(1)—C(19)	111.2(2)	C(3)—C(4)—C(5)	107.9(2)
C(3)—C(4)	1.453(2)	O(35)—N(2)—C(3)	126.6(2)	C(10)—N(9)—C(18)	117.3(2)
C(3)—C(10)	1.471(2)	O(35)—N(2)—C(1)	119.6(2)	N(9)—C(10)—C(11)	124.4(3)
C(4)—O(36)	1.210(2)	C(3)—N(2)—C(1)	113.7(2)	N(9)—C(10)—C(3)	115.1(2)
C(4)—C(5)	1.523(2)	N(2)—C(3)—C(4)	109.8(2)	C(11)—C(10)—C(3)	120.4(2)
C(6)—O(37)	1.205(2)				
N(33)—O(38)	1.215(3)				
N(33)—O(39)	1.221(3)				

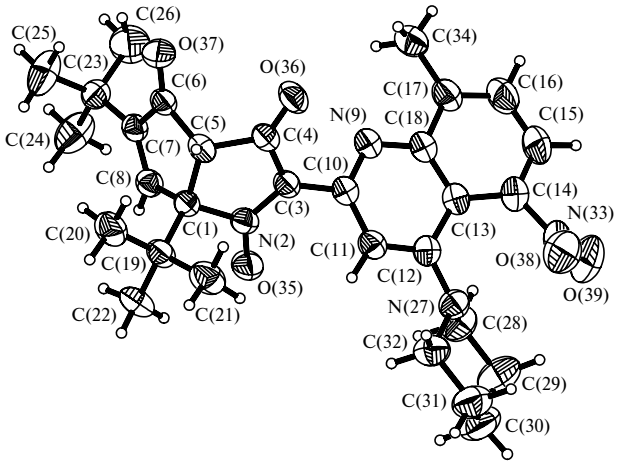


Fig. 10. Molecular structure of 1,7-di(*tert*-butyl)-3-(8-methyl-5-nitro-4-piperidinoquinolin-2-yl)-4,6-dioxo-2-azabicyclo-[3.3.0]octa-2,7-diene *N*-oxide (**16d**). Displacement ellipsoids are drawn at the 50% probability level. The angle between the C(1)N(2)C(3)C(4)C(5) and C(1)C(8)C(7)C(6)C(5) planes is 114.2°. The C(4)C(3)C(10)C(11) dihedral angle is 137.7(2)°.

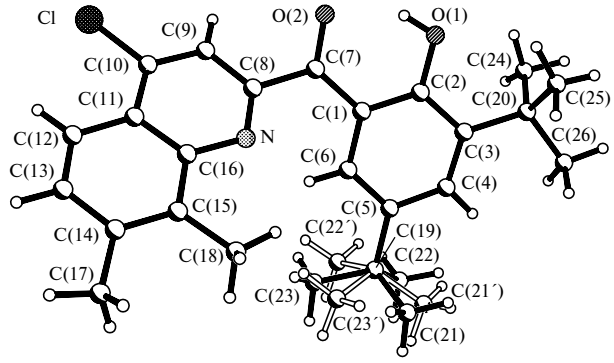
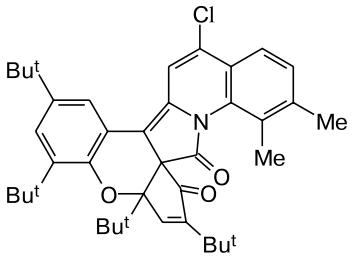


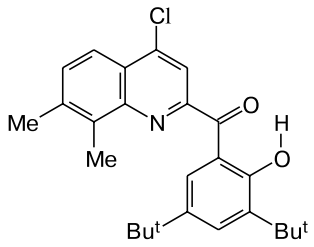
Fig. 11. Molecular structure of 4-chloro-2-(3,5-di-*tert*-butyl-2-hydroxybenzoyl)-7,8-dimethylquinoline (**21**). The O(1)...O(2) distance is 2.55 Å. The deviations of the O(1), C(7), O(2), and H(1) atoms from the plane through the C(1), C(2), C(3), C(4), C(5), and C(6) atoms are smaller than 0.05 Å. Two fragments are rotated about the C(7)—C(8) bond by the NC(8)—C(7)—C(1) angle of 39.2(2)°.

Table 16. Selected bond lengths (*d*) и bond angles (ω) for compound **21**

Bond	*d*/Å	Angle	ω/deg
O(1)—C(2)	1.342(3)	C(2)—O(1)—H(1)	108.0(2)
O(1)—H(1)	0.830(4)	C(8)—N—C(16)	118.4(2)
O(2)—C(7)	1.236(3)	C(2)—C(1)—C(6)	118.8(2)
N—C(8)	1.318(3)	C(2)—C(1)—C(7)	120.3(2)
N—C(16)	1.365(3)	C(6)—C(1)—C(7)	120.8(2)
C(1)—C(2)	1.403(4)	O(1)—C(2)—C(1)	120.4(2)
C(1)—C(6)	1.404(4)	O(2)—C(7)—C(1)	121.4(2)
C(1)—C(7)	1.464(4)	O(2)—C(7)—C(8)	115.7(2)
C(7)—C(8)	1.500(3)	C(1)—C(7)—C(8)	122.9(2)
		N—C(8)—C(9)	123.7(2)
		N—C(8)—C(7)	117.9(2)

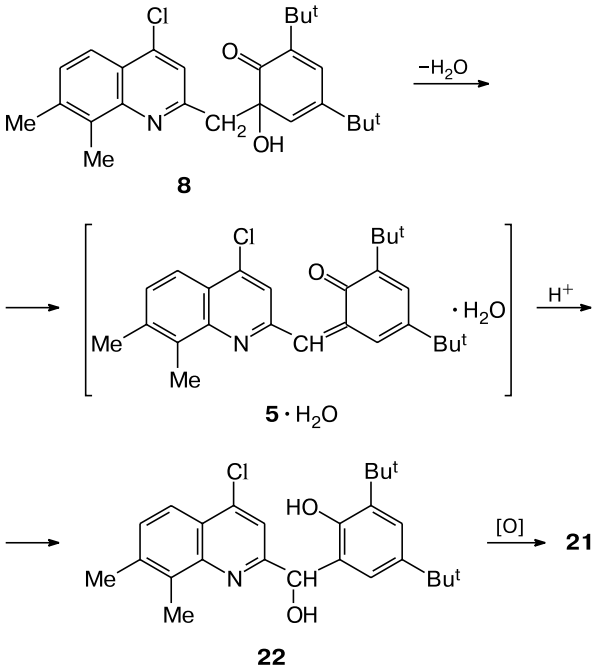


20



21

Scheme 7



(12.6 kcal mol^{-1} for structure **M5** deprived of all methyl and *tert*-butyl groups). Subsequent oxidation of **22** gives rise to ketone **21**.

Experimental

The ^{1}H and ^{13}C NMR spectra were recorded on Varian Unity 300 spectrometers. The ^{15}N NMR spectra were measured on a Bruker AM-500 spectrometer (500 MHz). The mass spec-

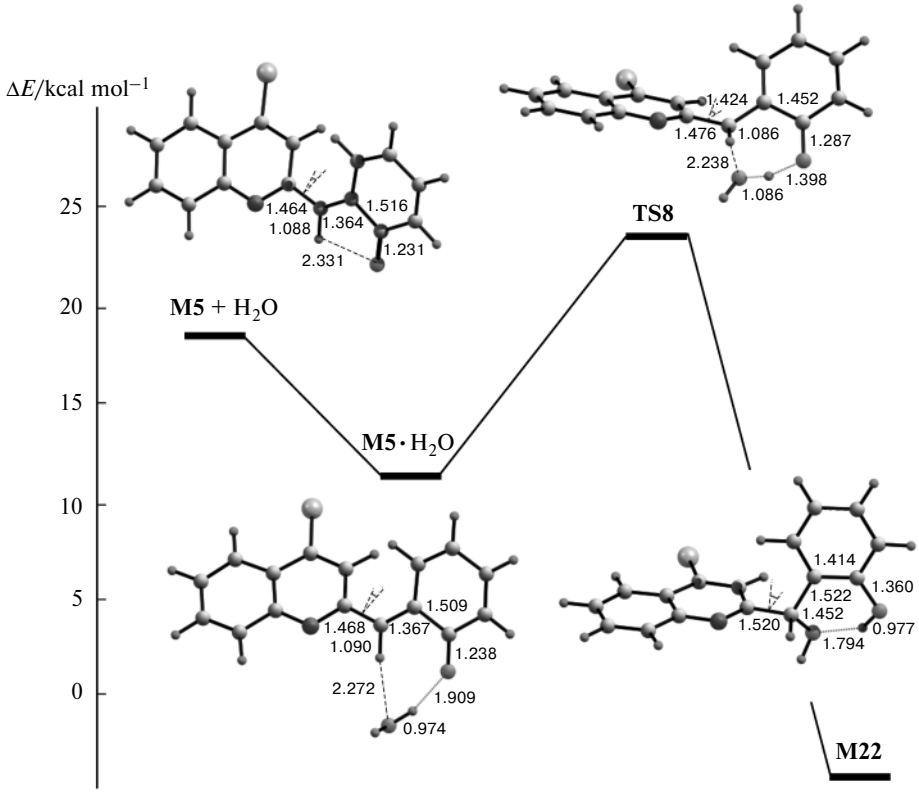


Fig. 12. Energy profile of the rearrangement of hydrated methylenequinone (**M5**) into carbinol (**M22**) calculated by the B3LYP/6-31G** method. The bond lengths are given in Å. The dihedral angles, deg: 30.8 (**M5**), 37.2 (**M5** · H_2O), 43.4 (**TS8**), and 71.9 (**M22**).

Table 17. Total energies (E_{tot}), the zero point energies (ZPE), and the relative energies (with the ZPE correction) of the structures corresponding to the stationary points on the potential energy surface for the reaction shown in Fig. 12

Structure	$-E_{tot}$*	ZPE	ΔE /kcal mol^{-1}
	au		
M5 + H_2O	1282.307526	0.237440	22.7
M5 · H_2O	1282.321137	0.240628	16.1
TS8	1282.300359(*i*582.6)	0.239877	28.7
M21	1282.35101	0.244960	0

* The imaginary vibrational frequency (cm^{-1}) for the structure of the transition state is given in parentheses.

tra were obtained on a Finnigan MAT INOS 50 mass spectrometer. The IR spectra were recorded on an IR-75 spectrometer as Nujol mulls. Chromatography was carried out on columns packed with Al_2O_3 (Brockmann activity II—III). The melting points were measured in glass capillaries on a PTP apparatus and are uncorrected. The starting 2-methylquinolines were synthesized according to procedures described earlier.[27,28]

Synthesis of 5,7-di(*tert*-butyl)-3-hydroxy-2-(quinolin-2-yl)tropones 6 and 7 (general procedures). ***Method A*. 5,7-Di(*tert*-butyl)-2-(4-chloro-8-methylquinolin-2-yl)-3-hydroxytropone (6e).** A mixture of 3,5-di(*tert*-butyl)-1,2-benzoquinone (**3**) (2.20 g, 10 mmol), 4-chloro-2,8-dimethylquinoline[27] (0.96 g, 5 mmol), and *p*-toluenesulfonic acid (0.20 g) was kept at 160—170 °C for 20 min. After cooling, the melt was dissolved in a 2 : 1 hexane—$CHCl_3$ mixture. The solution was passed through an alumina column (hexane—$CHCl_3$, 2 : 1, as the eluent), and a bright-yellow fraction was collected. Compound **6** was obtained in a yield of 0.22 g (11%) as yellow crystals, m.p. 189—191 °C (propan-2-ol).

***Method B*. 5,7-Di(*tert*-butyl)-2-(4-chloro-6,8-dimethylquinolin-2-yl)-3-hydroxytropone (6f).** A solution of 3,5-di(*tert*-butyl)-1,2-benzoquinone (**3**) (2.20 g, 10 mmol), 4-chloro-2,6,8-trimethylquinoline (1.03 g, 5 mmol), and *p*-toluenesulfonic acid (0.20 g) in *o*-xylene (10 mL) was refluxed for 6 h. After cooling, the solution was passed through an alumina column (hexane—$CHCl_3$, 2 : 1, as the eluent) and a bright-yellow fraction was collected. Compound **6f** was obtained in a yield of 0.55 g (26%) (**6f**) as yellow crystals, m.p. 198—201 °C (propan-2-ol).

5,7-Di(*tert*-butyl)-2-(4-chloro-6,8-dimethyl-5-nitroquinolin-2-yl)-3-hydroxy-4-nitrotropone (15g) and 5,7-di(*tert*-butyl)-2-(4-chloro-6,8-dimethyl-5-nitroquinolin-2-yl)-3-hydroxytropone (6j). A solution of 4,6-di(*tert*-butyl)-3-nitro-1,2-benzoquinone (**14**)[24] (2.65 g, 10 mmol), 4-chloro-2,6,8-trimethyl-5-nitroquinoline[28] (**4**) (1.03 g, 5 mmol), and *p*-toluenesulfonic acid (0.20 g) in *o*-xylene (10 mL) was refluxed for 1 h. After cooling, the solution was passed through an alumina chromatographic column (hexane—$CHCl_3$, 1 : 1, as the eluent) and two bright-yellow fractions were collected. Fraction I contained compound **6j**; fraction II, compound **15g**.

Compound **6j**, the yield was 0.07 g (3%), yellow crystals, m.p. 223—225 °C (propan-2-ol). Compound **15g**, the

yield was 0.154 g (6%), yellow crystals, m.p. 250—252 °C (propan-2-ol).

Method C. **5,7-Di(*tert*-butyl)-2-(4-chloro-7,8-dimethylquinolin-2-yl)-3-hydroxytropone (6g).** A solution of 3,5-di(*tert*-butyl)-1,2-benzoquinone (**3**) (4.40 g, 20 mmol) and 4-chloro-2,7,8-trimethylquinoline (2.05 g, 10 mmol) in AcOH (10 mL) was heated at 50 °C for 20 h and then kept at room temperature for 1 day. The precipitate of tropolone (**6g**) that formed was filtered off and washed with AcOH (10 mL) and water (100 mL). The yield of the precipitate was 1.8 g. The mother liquor was diluted with water, and the oily residue was extracted with chloroform (30 mL). The extract was washed with a sodium carbonate solution (3×50 mL) and water (3×50 mL) in a separating funnel and dried with anhydrous Na_2SO_4 for 3—4 h. The dry extract was passed through an alumina chromatographic column (hexane—$CHCl_3$, 1 : 1, as the eluent), and a bright-yellow fraction was collected. Compound **6g** was obtained in a yield of 0.87 g. The total yield was 2.67 g (63%), yellow crystals, m.p. 174—176 °C (propan-2-ol).

Method D. **5,7-Di(*tert*-butyl)-3-hydroxy-2-(8-methyl-4-morpholinoquinolin-2-yl)tropone (7a).** A solution of 5,7-di(*tert*-butyl)-2-(4-chloro-8-methylquinolin-2-yl)-3-hydroxytropone (**6e**) (0.3 g, 0.73 mmol) in a freshly distilled morpholine (3 mL) was refluxed for 1 h. The cooled solution was diluted with cold water. The precipitate that formed was filtered off, washed with warm water (200 mL), and dried. Compound **7a** was obtained in a yield of 0.3 g (89%) as yellow crystals, m.p. 200—202 °C (propan-2-ol).

4,7-Di(*tert*-butyl)-2-(4-chloro-8-methylquinolin-2-yl)-3-hydroxytropone (11) was synthesized by the reaction of 3,6-di(*tert*-butyl)-1,2-benzoquinone (**12**) (20 mmol) with 4-chloro-2,8-dimethylquinoline (**4**) (5 mmol) analogously to β-tropolone (**6f**) (method ***B***). The yield was 4%. Yellow crystals, m.p. 180—182 °C (propan-2-ol). ^{1}H NMR ($CDCl_3$), δ: 1.30 (s, 9 H, Bu^t(4)); 1.35 (s, 9 H, Bu^t(7)); 2.75 (s, 3 H, Me(8′)); 6.38 (d, 1 H, H(5), J = 8.0 Hz); 6.58 (d, 1 H, H(6), J = 8.0 Hz); 7.44 (t, 1 H, H(6′)); 7.6 (d, 1 H, H(7′)); 8.0 (d, 1 H, H(5′)); 8.26 (s, 1 H, H(3′)); 19.05 (s, 1 H, OH(3)). MS (EI, 70 eV), m/z (I_{rel} (%)): 409 $[M]^+$ (100), 394 (15), 381 (30), 366 (70), 338 (75), 57 (40), 41 (44). Found (%): C, 73.13; H, 6.80; Cl, 8.68; N, 3.42. $C_{25}H_{28}ClNO_2$. Calculated (%): C, 73.25; H, 6.88; Cl, 8.65; N, 3.42.

5,7-Di(*tert*-butyl)-3-hydroxy-4-nitro-2-(quinolin-2-yl)tropone (15a) and **5,7-di(*tert*-butyl)-2-(4-chlorobenzo[*h*]quinolin-2-yl)-3-hydroxy-4-nitrotropone (15b)** were synthesized by the reaction of 4,6-di(*tert*-butyl)-3-nitro-1,2-benzoquinone (**14**) (10 mmol) with the corresponding 2-methylquinoline (**4**) (5 mmol) analogously to β-tropolone **15g** (method ***B***).

1,7-Di(*tert*-butyl)-3-(6,8-dimethyl-4-morpholinoquinolin-2-yl)-4,6-dioxo-2-azabicyclo[3.3.0]octa-2,7-diene *N*-oxide (16b). A solution of 4,6-di(*tert*-butyl)-3-nitro-1,2-benzoquinone (**14**) (3.18 g, 12 mmol), 2,6,8-trimethyl-4-morpholinoquinoline (2.56 g, 10 mmol), and *p*-toluenesulfonic acid (0.50 g) in *o*-xylene (10 mL) was refluxed for 1 h. After cooling, the solution was passed through an alumina chromatographic column ($CHCl_3$ as the eluent) and a yellow fraction was collected. Compound **16b** was obtained in a yield of 1.31 g (26%) as yellow crystals, m.p. 220—222 °C (propan-2-ol). ^{13}C NMR ($CDCl_3$), δ: 18.0, 22.1, 25.9, 28.1, 32.7, 36.6, 52.6, 60.8, 66.8, 87.3, 108.7, 119.8, 123.1, 131.7, 136.5, 137.8, 138.8, 143.5, 147.0, 149.4, 156.2, 158.0, 185.3, 196.6. ^{15}N NMR ($CDCl_3$), δ: 42.05, 277.53, 324.60.

4-Chloro-2-(3,5-di-*tert*-butyl-2-hydroxybenzoyl)-7,8-dimethylquinoline (21) and 8,9a,11,13-tetra(*tert*-butyl)-16-chloro-3,4-dimethylcyclopenta-[2′,3′]chromeno[4′,3′,3,4]pyrrolo[1,2-*a*]quinoline-6,7(9a*H*)dione (20). A solution of 3,5-di(*tert*-butyl)-1,2-benzoquinone (**3**) (2.20 g, 10 mmol), 4-chloro-2,7,8-trimethylquinoline (1.03 g, 5 mmol), and *p*-toluenesulfonic acid (0.20 g) in *o*-xylene (10 mL) was refluxed as described in the method ***B***. After cooling, the solution was passed through an alumina chromatographic column (hexane—$CHCl_3$, 10 : 1, as the eluent), and the first two fractions eluted prior to the bright-yellow fraction of tropolone (**6g**) were collected. The first pale-yellow fraction contained compound **21**; the second orange fraction, compound **20**. Compound **21**, the yield was 0.22 g (10%). Yellow crystals, m.p. 144—145 °C (propan-2-ol). IR, ν/cm^{-1}: 1607, 1580, 1540, 1500, 1473, 1406, 1367, 1353, 1340, 1287, 1260, 1233. ^{1}H NMR ($CDCl_3$), δ: 1.29 (s, 9 H, Bu^t(5)); 1.50 (s, 9 H, Bu^t(3)); 2.56 (s, 3 H, Me(7′)); 2.77 (s, 3 H, Me(8′)); 7.59 (d, 1 H, H(6′), J = 8.5 Hz); 7.64 (d, 1 H, H(4), J = 2.4 Hz); 8.00 (s, 1 H, H(3′)); 8.09 (d, 1 H, H(5′), J = 8.5); 8.20 (d, 1 H, H(6), J = 2.4 Hz); 12.92 (s, 1 H, OH(2)). Found (%): C, 73.57; H, 6.98; Cl, 8.18; N, 3.22. $C_{26}H_{30}ClNO_2$. Calculated (%): C, 73.66; H, 7.13; Cl, 8.36; N, 3.30. Compound **20**, the yield was 0.18 g (6%). Orange crystals, m.p. 216—218 °C (propan-2-ol). ^{1}H NMR ($CDCl_3$), δ: 1.00 (s, 9 H, Bu^t(9)); 1.29 (s, 9 H, Bu^t(7)); 1.32 (s, 9 H, Bu^t(5a)); 1.43 (s, 9 H, Bu^t(4)); 2.31 (s, 3 H, Me(15)); 2.35 (s, 3 H, Me(16)); 6.70 (s, 1 H); 7.03 (m, 3 H); 7.23—7.24 (m, 2 H). Found (%): C, 76.54; H, 7.53; Cl, 5.32; N, 2.12. $C_{40}H_{48}ClNO_3$. Calculated (%): C, 76.71; H, 7.73; Cl, 5.66; N, 2.24.

X-ray diffraction study. X-ray diffraction data sets were collected on an automated KUMA-DIFFRACTION KM-4 diffractometer at room temperature (Mo-Kα radiation, ω/2 scanning technique, graphite monochromator). All structures were solved by direct methods with the use of the SHELXS-97 program package[29] and refined by the full-matrix least-squared method with anisotropic displacement parameters for nonhydrogen atoms. All hydrogen atoms, except for the hydrogen atoms of the *tert*-butyl group of compound **7a** (high temperature vibration) and the *tert*-butyl group of compound **21** (disorder in a ratio of 1 : 1), were located in difference electron density maps. The atomic coordinates, complete tables of the bond lengths, bond angles, and atomic displacement parameters for compounds **6e**, **7a**, **8**, **16b**, **16d**, and **21** were deposited with the Cambridge Structural Database (CCDC 607742 (**6e**), 299736 (**7a**), 299737 (**8**), 299738 (**16b**), 299739 (**16d**), and 299740 (**21**)). Principal crystallographic parameters of compounds **6e**, **7a**, **8**, **16b**, **16d**, and **21** are given in Table 18.

Calculation methods. All calculations were carried out with the use of the B3LYP hybrid functional, including Becke's three-parameter exchange functional[30,31] and the Lee—Yang—Parr correlation functional,[32] and the 6-31G** basis set with the use of the GAUSSIAN 03 program package.[33] The nature of the stationary points on the potential energy surface was characterized based on analysis of the force constant matrix (Hesse matrix). The zero-point corrections were calculated from analytical vibrational frequencies without additional scaling. The energies of monomer dimerization were calculated as the difference between the energy of the dimer and the sum of the energies of the monomers without basis set superposition error (BSSE).[34]

Table 18. Crystallographic data for compounds **6e**, **7a**, **8**, **16b**, **16d**, and **21**

Compound	**6e**	**7a**	**8**	**16b**	**16d**	**21**
Molecular formula	$C_{25}H_{28}NOCl$	$C_{29}H_{36}N_2O_3$	$C_{26}H_{32}NO_2Cl$	$C_{30}H_{37}N_3O_4$	$C_{30}H_{36}N_4O_5$	$C_{26}H_{30}NO_2Cl$
Molecular weight	409.93	460.60	425.98	503.63	532.63	423.96
Crystal system	Monoclinic	Triclinic	Triclinic	Triclinic	Triclinic	Triclinic
Space group	$P2_1/c$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a/Å	14.057(8)	11.602(6)	10.907(3	9.946(2)	10.055(2)	10.699(5)
b/Å	13.199(9)	17.326(8)	13.014(4	12.260(2)	11.376(1)	18.686(9)
c/Å	11.923(7)	14.355(6)	10.808(6)	13.042(3)	14.489(3)	6.800(6)
α/deg	90	99.66(4)	109.85(4)	110.72(3)	67.38(2)	81.80(7)
β/deg	90.95(5)	105.73(5)	112.65(4)	90.06(4)	74.17(2)	68.50(7)
γ/deg	90	102.82(5)	103.14(3)	109.14(3)	74.41(2)	71.61(5)
V/Å^3	2212(2)	2627(2)	1213.1(8)	1393.1(5)	1446.6(4)	1199.7(13)
Z	4	4	2	2	2	2
D/g cm^{-3}	1.231	1.165	1.166	1.201	1.223	1.174
μ/mm^{-1}	0.193	0.075	0.178	0.080	0.084	0.180
Scan range	1.45—26.09	1.24—25.07	1.83—25.06	1.68—25.17	1.55—22.47	2.12—23.05
Number of measured reflections	3459	6681	3178	4930	3768	3335
Number of reflections with $I > 2\sigma(I)$	2446	3867	1300	2466	3169	2109
Number of parameters in refinement	265	601	275	350	368	317
R	0.045	0.057	0.079	0.058	0.044	0.048
R_w	0.072	0.128	0.221	0.164	0.052	0.099
Radiation	Mo-Kα	Mo-Kα	Mo-Kα	Mo-Kα	Mo-Kα	Mo-Kα
GOOF	1.107	1.068	0.946	1.119	1.045	0.958

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