

THE REACTION OF QUADRICYCLANE WITH *p*-ANILS

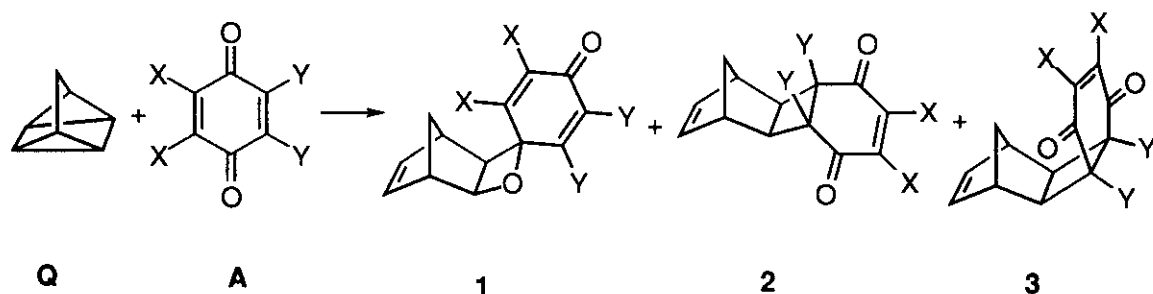
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Abstract-----The reaction of quadricyclane (**Q**) with *p*-anils has been generalized in order to define its scope. Tetrafluoro-, tetrachloro-, and tetrabromo-*p*-benzoquinones in dichloromethane or chloroform, at or below room temperature give predominant or exclusive formation of the adduct to the C=O bond of the quinone as confirmed by the X-ray structure of the adduct to chloranil. In the case of DDQ (dicyanodichloro-*p*-benzoquinone), the major product is the standard [4+2]-cycloadduct, while the adduct to the C=O bond is formed as minor product and adds to a second molecule of quadricyclane to form bis-adduct (**4**). The structure of the latter has also been defined by X-ray analysis.

In the course of an investigation aimed to the synthesis of C₂-symmetric chiral ketones² we wanted to prepare the double adduct of quadricyclane (**Q**) to *p*-anils (**A**) (*i.e.* tetrafluoro, tetrachloro, and tetrabromo) as well as with DDQ (dicyanodichloro-*p*-benzoquinone), in similarity to the double adduct of the parent *p*-benzoquinone.^{2,3} In the literature it has been reported that *p*-chloranil forms with quadricyclane a charge transfer complex⁴ and that converts it photochemically to norbornadiene.⁵ Except for a recent report by Hirao *et al.*,^{6,7} no indication on the formation of adducts has ever been reported. Indeed, virtually no reaction was observed when quadricyclane and *p*-chloranil were mixed at room temperature in acetonitrile under the conditions of the photochemical isomerisation, except for a slow conversion of **Q** into norbornadiene (**N**). Differently, however, a clean reaction occurs when the two reagents are mixed in dichloromethane or chloroform with formation of a highly predominant product plus two other minor compounds as observed in the ¹H nmr spectrum of the crude reaction mixture. The predominant product presents analytical data in accordance with a 1:1 adduct to which was assigned, in similarity to the work of Hirao,⁷ structure (**1**) on the basis of the ¹H nmr spectrum, decoupling experiments, considerations on the size of the coupling constants and NOE experiments. An X-ray analysis on the tetrachloro adduct (Figure 1) allowed to confirm the structure assignment.

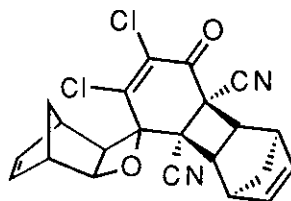


The two minor products present ^1H nmr data in agreement with the expected, symmetrical Diels-Alder adducts (**2**) and (**3**) (Table 1).

Table 1. Reaction conditions and product composition (ratio as determined by ^1H nmr of the crude reaction mixture) in the reaction of *p*-benzoquinones with quadricyclane.

<i>p</i> -Quinone	Solvent	Temp. ($^{\circ}\text{C}$)	1	2	3
X = Y = H ^{2,3}	neat	90	-	100	-
X = Y = F	CH ₂ Cl ₂	0	75	15	10
X = Y = Cl	CH ₂ Cl ₂	25	80	15	5
X = Y = Br	CH ₂ Cl ₂	25	40	10	-
X = Cl; Y = CN	CH ₂ Cl ₂	40	-	50	traces

Comparatively to *p*-chloroanil, the reaction of the tetrafluoro derivative occurs more rapidly and cooling of the reaction mixture to 0 $^{\circ}\text{C}$ is necessary for a cleaner addition. The reaction of the tetrabromo compound expectedly occurs at a lower rate and takes several hours at room temperature. In every case, the major product obtained is adduct (**1**) and smaller amounts of the standard Diels-Alder adducts to the C-C double bond of the quinone (*i.e.* **2** and **3**), as gained by nmr (Table 1). In the case of DDQ (dicyanodichloro-*p*-benzoquinone), the symmetrical cycloadduct (**2**) (X = Cl, Y = CN) is obtained as predominant product together with traces of **3** (X = Cl, Y = CN). The adduct corresponding to **1** with DDQ was not observed, instead, small quantities of adduct (**4**) were isolated.



The latter may derive from a second cycloaddition of **Q** to **1** ($X = \text{Cl}$, $Y = \text{CN}$) which is formed as primary product. The structure of compound (**4**) was firmly established by means of diffractometric analysis (Figure 1).

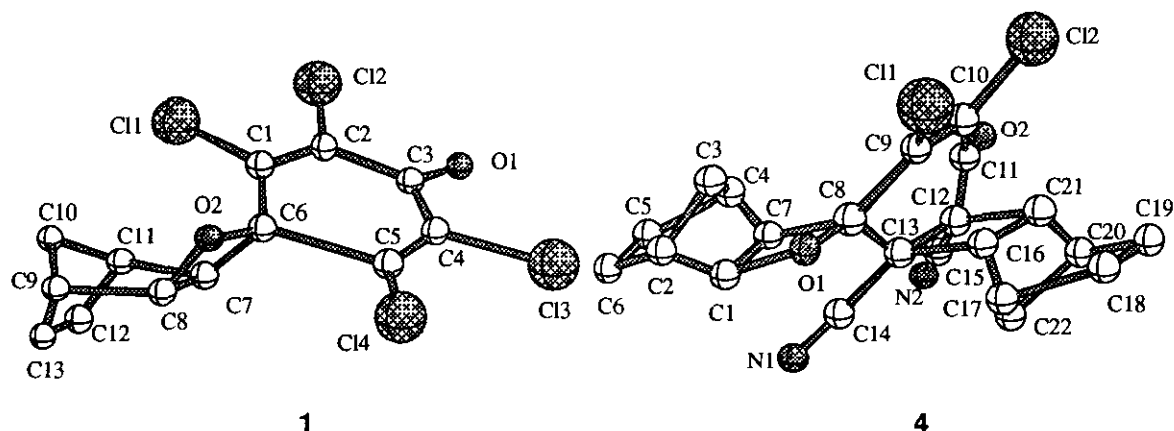
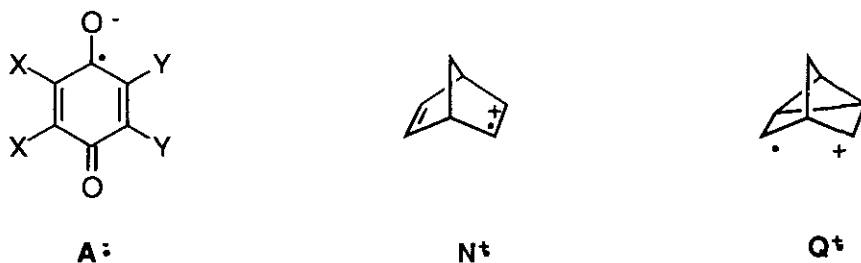


Figure 1. Perspective representation of (**1**) ($X = Y = \text{Cl}$) and (**4**) showing all non-hydrogen atoms.

The reason of the different behavior observed with the changing of the solvent (the reaction occurs in CH_2Cl_2 while in CH_3CN **Q** is converted into **N**) is attributed to the different species involved in the different media. It is possible that in the more polar acetonitrile, the radical ions are solvated and thus dissociate into free ions which separately collapse without addition, while in the less polar solvents are as tight ion pairs and thus can convert into addition products within the solvent cage.⁵ On the nature of the radical ions, it is reasonable to suppose the formation of **A** \cdot as the radical cation of the benzoquinone⁸ and of **Q** \cdot^+ as that derived from quadricyclane. The latter radical cation **Q** \cdot^+ rearranges rapidly⁵ into **N** \cdot^+ before adding to **A** \cdot to form **1**.

It is worth mentioning that we have tried to generate in an alternative way **N** \cdot^+ , *i.e.* via photoelectron transfer from norbornadiene by photoexcited *p*-chloranil,⁹ but we failed to observe cycloadduct (**1**). The reason for this apparent discrepancy may be found in the photogeneration of a triplet exiplex which, differently from the ground-state species, gives a reverse electron transfer and diffuses apart rather than bonding to **1**. The generation of **N** \cdot^+ in the singlet state is prevented by chloranil itself that shields the excitation of other sensitizers (1-cyanonaphthalene, for example).^{5,8}



It should be recalled that the formation of cycloadducts of type (1) is known to be produced in the photochemical reaction of quadricyclane with *p*-benzoquinone¹⁰ and that similar adducts are also formed in the photoaddition of others ketones.¹¹ Carbonyl groups containing an electron-withdrawing group at the α -position are also capable of thermal cycloaddition to quadricyclane.¹² Eventually, it should also be noticed that the reaction of heavily substituted quadricyclanes has been recently reported to give different products¹³ and also that the reaction of the ortho isomer (*o*-chloranil) with quadricyclane has also been investigated.¹⁴ In view of the large amount of work that has been done on this reaction and on the importance that it may assume as a way of solar energy storage, the formation of the adduct described here in the thermal reaction is of interest.

EXPERIMENTAL

Melting points are uncorrected. The ¹H nmr and ¹³C nmr spectra were recorded on a Bruker AC 200 operating at 200 MHz and 50 MHz respectively with tetramethylsilane as internal standard. The ir spectra were performed with a Perkin Elmer 683 spectrophotometer. Flash chromatography was performed with Merk silica gel 60 (230-400 Mesh). Known compounds used in this research were either purchased from standard chemical suppliers or prepared according to literature procedures and purified to match reported physical and spectral data. Quadricyclane was kindly provided us by Dr. Nereo Nodari (Enichem Synthesis).

Cycloaddition of p-Chloranil to Quadricyclane. Quadricyclane (2.2 g, 23.9 mmol) was added to a rapidly stirred mixture of *p*-chloranil (2.44 g, 10 mmol) in dry dichloromethane (10 ml) under nitrogen at 0 °C in a light-protected vessel. The reaction mixture was stirred at room temperature until the solid disappeared (60 h). After concentration at reduced pressure, the crude was purified by flash chromatography on silica gel (eluant dichloromethane - *n*-hexane 3:7).

1 (X = Y = Cl): (50%). mp 210 °C (decomp.) (from dichloromethane/*n*-hexane). ¹H Nmr (CDCl₃) δ 1.56 (1 H, d, 1/2 AB system, $J = 9.9$ Hz), 2.58 (1 H, d, 1/2 AB system, $J = 4.9$ Hz), 3.08 (1 H, s), 3.14 (1 H, d, 1/2 AB system, $J = 9.9$ Hz), 3.33 (1 H, s), 4.97 (1 H, d, $J = 4.9$ Hz), 5.92 (1 H, dd, $J = 5.6$ and 3.3 Hz), 6.22 (1 H, dd, $J = 5.6$ and 3.3 Hz); ¹³C nmr (CDCl₃) δ 42.79, 42.87, 45.48, 54.69, 82.49, 84.47, 128.66, 130.92, 133.44, 140.82, 150.60, 157.91, 170.32; ir (KBr) ν 3060, 2985, 1670, 1555, 1110, 940, 735 cm⁻¹. Anal. Calcd for C₁₃H₈O₂Cl₄: C, 46.2; H, 2.4. Found: C, 45.8; H, 2.4.

Crystal data; Suitable crystals were obtained by slow evaporation from a dichloromethane solution. C₁₃H₈O₂Cl₄ crystallized in the monoclinic system, space group $P2_1/n$, $a = 8.030(1)$, $b = 16.768(2)$, $c = 10.467(2)$ Å, $\beta = 108.2(1)^\circ$, $V = 1339$ Å³, $Z = 4$, $D_c = 1.69$ g cm⁻³. 3429 Reflections were collected on a four-circle Philips PW 1100 diffractometer up to $\theta = 28^\circ$, θ - $2\theta =$ scan mode, Mo- K_α monochromatized radiation ($\lambda = 0.7107$ Å). The structure was solved by

direct methods using the phasing program 'Multan', and refined by block-diagonal least squares with anisotropic thermal parameters for non-hydrogen atoms. Hydrogen atoms were found on a ΔF map, but not refined. The final R factor for 1824 observed reflections [$F > 5\sigma(F)$] was 0.067. The structure was solved by direct methods using the program SHELX86.¹⁵ SHELX76 was used for refinement calculations. Further data are provided in Tables I-III.

Table I. Positional and thermal ($\text{\AA}^2 \times 10^3$) parameters for cycloadduct (1) ($X = Y = \text{Cl}$). Standard deviations are given in parentheses. Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

Atom	x	y	z	U_{eq}	Atom	x	y	z	U_{eq}
Cl(1)	0.2014(2)	0.7637(9)	0.7976(1)	0.0573(5)	C(5)	0.6390(6)	0.6321(3)	0.8643(5)	0.0390(1)
Cl(2)	0.2368(2)	0.6830(1)	1.0741(1)	0.0578(5)	C(6)	0.4605(6)	0.6603(3)	0.7723(4)	0.0360(1)
Cl(3)	0.8481(2)	0.5542(1)	1.0791(2)	0.0703(6)	C(7)	0.3946(6)	0.5910(3)	0.6633(5)	0.0430(1)
Cl(4)	0.8073(2)	0.6311(1)	0.7941(2)	0.0600(5)	C(8)	0.4389(7)	0.6499(3)	0.5659(6)	0.0520(2)
O(1)	0.5238(6)	0.5659(2)	1.1478(4)	0.0600(2)	C(9)	0.2716(9)	0.6556(4)	0.4452(6)	0.0640(2)
O(2)	0.4689(5)	0.7158(2)	0.6695(3)	0.0470(1)	C(10)	0.1271(9)	0.6499(4)	0.5157(6)	0.0740(3)
C(1)	0.3496(5)	0.6885(3)	0.8575(5)	0.0370(1)	C(11)	0.2013(7)	0.5722(4)	0.5945(6)	0.0570(2)
C(2)	0.3696(6)	0.6574(3)	0.9794(4)	0.0390(1)	C(12)	0.2141(8)	0.5244(4)	0.4732(6)	0.0610(2)
C(3)	0.5155(7)	0.6023(3)	1.0451(5)	0.0420(1)	C(13)	0.2570(1)	0.5719(4)	0.3893(6)	0.0690(3)
C(4)	0.6592(6)	0.6004(3)	0.9855(5)	0.0440(2)					

Table II. Interatomic distances (\AA) for cycloadduct (1) ($X = Y = \text{Cl}$). Standard deviations are given in parentheses.

Cl(1)-C(1)	1.713(5)	Cl(2)-C(2)	1.722(6)	Cl(3)-C(4)	1.713(5)	Cl(4)-C(5)	1.728(6)
O(1)-C(3)	1.220(7)	O(2)-C(6)	1.441(6)	O(2)-C(8)	1.513(6)	C(1)-C(2)	1.340(7)
C(1)-C(6)	1.519(7)	C(2)-C(3)	1.481(6)	C(3)-C(4)	1.474(8)	C(4)-C(5)	1.337(7)
C(5)-C(6)	1.531(6)	C(6)-C(7)	1.599(6)	C(7)-C(8)	1.539(8)	C(7)-C(11)	1.526(7)
C(8)-C(9)	1.533(8)	C(9)-C(10)	1.560(1)	C(9)-C(13)	1.511(9)	C(10)-C(11)	1.558(9)
C(11)-C(12)	1.530(1)	C(12)-C(13)	1.310(1)				

Table III. Bond angles (deg) for cycloadduct (1) ($X = Y = \text{Cl}$). Standard deviations are given in parentheses.

C(6)-O(2)-C(8)	91.7(3)	Cl(1)-C(1)-C(6)	118.8(3)	Cl(1)-C(1)-C(2)	119.8(4)
C(2)-C(1)-C(6)	121.3(4)	Cl(2)-C(2)-C(1)	122.7(4)	C(1)-C(2)-C(3)	121.8(5)
Cl(2)-C(2)-C(3)	115.4(4)	O(1)-C(3)-C(2)	122.6(5)	C(2)-C(3)-C(4)	115.2(4)
O(1)-C(3)-C(4)	121.9(5)	Cl(3)-C(4)-C(3)	116.0(4)	C(3)-C(4)-C(5)	120.9(5)
Cl(3)-C(4)-C(5)	123.1(5)	Cl(4)-C(5)-C(4)	121.3(5)	C(4)-C(5)-C(6)	122.1(5)
Cl(4)-C(5)-C(6)	116.0(4)	C(1)-C(6)-C(5)	109.4(4)	O(2)-C(6)-C(5)	114.6(4)
O(2)-C(6)-C(1)	114.2(4)	C(5)-C(6)-C(7)	105.1(4)	C(1)-C(6)-C(7)	121.4(5)
O(2)-C(6)-C(7)	91.1(3)	C(6)-C(7)-C(11)	123.2(5)	C(6)-C(7)-C(8)	85.0(4)
C(8)-C(7)-C(11)	103.4(4)	O(2)-C(8)-C(7)	90.8(4)	C(7)-C(8)-C(9)	105.2(5)
O(2)-C(8)-C(9)	116.6(5)	C(8)-C(9)-C(13)	101.8(5)	C(8)-C(9)-C(10)	101.3(5)
C(10)-C(9)-C(13)	98.5(6)	C(9)-C(10)-C(11)	94.8(6)	C(7)-C(11)-C(10)	104.0(5)
C(10)-C(11)-C(12)	96.5(5)	C(7)-C(11)-C(12)	100.2(5)	C(11)-C(12)-C(13)	109.7(6)
C(9)-C(13)-C(12)	108.1(6)				

2 ($X = Y = \text{Cl}$): (15 %). mp 224 °C (decomp.) (from dichloromethane/ hexane). ^1H Nmr (CDCl_3) δ 1.52 (1 H, d, 1/2 AB system, $J = 10.0$ Hz), 2.37 (1 H, d, 1/2 AB system, $J = 10.0$ Hz), 2.53 (2 H, s), 3.19 (2 H, br s), 6.18 (2 H, br s); ^{13}C nmr (CDCl_3) δ 43.54, 43.89, 45.61, 68.07, 137.71, 144.83, 182.03; ir (KBr) ν 2981, 1712, 1191, 789, 678 cm^{-1} . Anal. Calcd for $\text{C}_{13}\text{H}_8\text{O}_2\text{Cl}_4$: C, 46.2; H, 2.4. Found: C, 46.4; H, 2.4.

3 ($X = Y = \text{Cl}$): (5 %). mp 147-148 °C (from dichloromethane/ hexane). ^1H Nmr (CDCl_3) δ 0.55 (1 H, d, 1/2 AB system, $J = 12.5$ Hz), 1.37 (1 H, dt, 1/2 AB system, $J = 12.5$ and 1.5 Hz), 2.82 (2

H, s), 3.27 (2 H, s), 6.10 (2 H, s); ^{13}C nmr (CDCl_3) δ 42.33 (2 C), 49.28, 64.03, 136.59, 145.41, 180.88; ir (KBr) ν 2968, 1710, 1209, 689 cm^{-1} . Anal. Calcd for $\text{C}_{13}\text{H}_8\text{O}_2\text{Cl}_4$: C, 46.2; H, 2.4. Found: C, 46.4; H, 2.4.

Cycloaddition of p-Fluoranil and p-Bromanil to Quadricyclane. The same procedure described for *p*-chloranil was applied for the preparation of the tetrafluoro- and tetrabromo-*p*-benzoquinone adducts (*cf.* Table 1 for reaction conditions):

1 (X = Y = F): (75%). Purified by kugelrohr distillation at 120 °C/0.5 torr. ^1H Nmr (CDCl_3) δ 1.64 (1 H, d, 1/2 AB system, $J = 9.4$ Hz), 2.71 (1 H, d, 1/2 AB system, $J = 9.4$ Hz), 2.77 (1 H, d, $J = 4.7$ Hz), 3.24 (1 H, br s), 3.27 (1 H, br s), 4.89 (1 H, br s), 5.90 (1 H, dd, $J = 5.2$ and 4.0 Hz), 6.25 (1 H, dd, $J = 5.2$ and 3.2 Hz); ^{13}C nmr (CDCl_3) δ 41.60, 41.93, 42.41, 45.73, 46.62, 83.04, 132.91, 136.78 (dm, $J = 267.0$ Hz), 139.03 (dm, $J = 264.0$ Hz), 140.64, 152.47 (dm, $J = 287.0$ Hz), 155.60 (dm, $J = 287.0$ Hz), 171.54 (m); ir (KBr) ν 2985, 1700, 1670, 1300, 875, 720 cm^{-1} . Anal. Calcd for $\text{C}_{13}\text{H}_8\text{O}_2\text{F}_4$: C, 57.4; H, 3.0. Found: C, 57.5; H, 3.2.

2 and 3 (X = Y = F): (20%). ^1H Nmr (CDCl_3 , mixture of **2** and **3** in 2:1 ratio) δ -0.5 (1 H, d, 1/2 AB system, $J = 11.2$ Hz, **3**), 1.40 (1 H, d, 1/2 AB system, $J = 11.2$ Hz, **2**), 1.50 (1 H, d, 1/2 AB system, $J = 11.2$ Hz, **3**), 2.08 (1 H, d, 1/2 AB system, $J = 11.2$ Hz, **2**), 2.45-2.70 (4 H, m, 2 isomers), 3.26 (2 H, s, **3**), 3.30-3.45 (2 H, m, **2**), 6.10 (2 H, s, **3**), 6.20 (2 H, s, **2**); ir (KBr, as mixture of **2** and **3** in 2:1 ratio) ν 3010, 2926, 2866, 1739, 1362, 765, 727 cm^{-1} . Anal. Calcd for $\text{C}_{13}\text{H}_8\text{O}_2\text{F}_4$ (as mixture of **2** and **3** in 2:1 ratio): C, 57.4; H, 3.0. Found: C, 57.5; H, 3.1.

1 (X = Y = Br): (40 %). mp 145 °C (decomp.) (from dichloromethane/ hexane). ^1H Nmr (CDCl_3) δ 1.63 (1 H, d, 1/2 AB system, $J = 10.9$ Hz), 2.53 (1 H, d, $J = 5.1$ Hz), 3.05 (1 H, br s), 3.11 (1 H, d, 1/2 AB system, $J = 10.9$ Hz), 3.33 (1 H, br s), 4.90 (1 H, d, $J = 5.1$ Hz), 5.91 (1 H, dd, $J = 5.5$ and 3.2 Hz), 6.18 (1 H, dd, $J = 5.5$ and 3.0 Hz); ^{13}C nmr (CDCl_3) δ 42.89, 43.42, 45.52, 55.86, 81.91, 86.85, 123.14, 125.31, 133.24, 140.34, 148.46, 157.50, 172.00; ir (KBr) ν 2956, 2866, 1667, 1065, 716, 641 cm^{-1} . Anal. Calcd for $\text{C}_{13}\text{H}_8\text{O}_2\text{Br}_4$: C, 30.5; H 1.6. Found: C, 30.7; H, 1.4.

2 (X = Y = Br): (10%). mp 223 °C (decomp.) (from dichloromethane/ hexane). ^1H Nmr (CDCl_3 ,) δ 1.43 (1 H, d, 1/2 AB system, $J = 10.4$ Hz), 2.34 (1 H, d, 1/2 AB system, $J = 10.4$ Hz), 2.69 (2 H, s), 3.08 (2 H, s), 6.21 (2 H, s); ^{13}C nmr (CDCl_3) δ 43.68, 45.05, 45.51, 137.61, 140.08, 181.40, 186.43. ir (KBr) ν 2983, 1697, 1189, 738, 687, 626 cm^{-1} . Anal. Calcd for $\text{C}_{13}\text{H}_8\text{O}_2\text{Br}_4$: C, 30.5; H 1.6. Found: C, 30.5; H, 1.6.

Cycloaddition of p-dichlorodicyanoquinone (DDQ) to Quadricyclane. Quadricyclane (220 mg, 2.4 mmol) was added to a stirred mixture of DDQ (500 mg, 2.2 mmol) in dry dichloromethane (5 ml) under nitrogen in a light-protected vessel. The mixture was stirred at reflux temperature (40 °C) until the solid disappeared (72 h). The reaction mixture was concentrated in *vacuum* and purified by flash chromatography with an hexane-ethyl acetate mixture (4:1) as eluant.

2 (X = Cl; Y = CN): (50%). mp 260 °C (CHCl₃/*n*-hexane) (decomp.). ¹H Nmr (acetone-d₆) δ 1.73 (1 H, d, *J* = 12.0 Hz), 2.41 (1 H, d, *J* = 12.0 Hz), 2.69 (2 H, s), 3.25 (2 H, s), 6.20 (2 H, s); ¹³C nmr (acetone-d₆) δ 42.42, 44.11, 44.30, 49.36, 114.08, 173.32, 144.62, 179.90; ir (KBr) ν 3000, 2240, 1705, 1560, 1210, 1170 cm⁻¹. Anal. Calcd for C₁₅H₈N₂O₂Cl₂: C, 56.4; H 2.5; N, 8.8. Found: C, 56.3; H, 2.6; N 8.6.

4 (X = CN; Y = Cl): (8 %). mp 267-269 °C (CHCl₃/ ethyl acetate). ¹H Nmr (CDCl₃) δ 1.55 (1 H, d, 1/2 AB system, *J* = 11.2 Hz), 1.78 (1 H, d, 1/2 AB system, *J* = 12.0 Hz), 1.95 (1 H, d, *J* = 7.5 Hz), 2.13 (1 H, d, *J* = 7.5 Hz), 2.41 (1 H, d, 1/2 AB system, *J* = 11.2 Hz), 2.50 (1 H, d, 1/2 AB system, *J* = 12.0 Hz), 2.63 (1 H, d, *J* = 5.0 Hz), 2.85 (1 H, s), 3.20 (1 H, s), 3.25 (2 H, br s), 4.90 ((1 H, d, *J* = 5.0 Hz), 5.85-6.00 (1 H, m), 6.05-6.30 (3 H, m); ¹³C nmr (CDCl₃) δ 40.87, 41.71, 42.45, 42.90, 43.09, 43.73, 44.25, 45.64, 47.52, 49.77, 50.37, 82.61, 83.13, 112.24, 115.37, 132.50, 136.15, 137.09 (2 C), 139.46, 148.22, 179.66; ir (KBr) ν 3067, 2982, 2253, 1712, 1579, 1326, 891, 716 cm⁻¹. Anal. Calcd for C₂₂H₁₆N₂O₂Cl₂: C, 64.2; H 3.9; N, 6.8. Found: C, 64.4; H, 4.0; N 6.9.

Crystal data; Suitable crystals were obtained by slow evaporation from a dichloromethane solution. C₂₂H₁₆O₂Cl₂N₂ crystallized in the monoclinic system, space group *P*2_{1/n} *a* = 16.461(2), *b* = 13.344(2), *c* = 8.681(2) Å, β = 104.4(2)°, *V* = 1847 Å³, *Z* = 4, *D_c* = 1.48 g cm⁻³. 4727 Reflections were collected on a four-circle Philips PW 1100 diffractometer up to θ = 28°, θ-2θ = scan mode, Mo-*K*_α monochromatized radiation (λ = 0.7107 Å). The structure was solved by direct methods using the phasing program 'Mltan', and refined by block-diagonal least squares with anisotropic thermal parameters for non-hydrogen atoms. Hydrogen atoms were found on a Δ*F* map, but not refined. The final *R* factor for 3090 observed reflections [*F* > 5σ(*F*)] was 0.039. The structure was solved by direct methods using the program SHELX86.¹⁵ SHELX76 was used for refinement calculations. Further data are provided in Tables IV-VI.

Table IV. Positional and thermal (Å²×10³) parameters for cycloadduct (4). Standard deviations are given in parentheses. Equivalent isotropic *U* defined as one third of the trace of the orthogonalized *U_{ij}* tensor.

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U_{eq}</i>	Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U_{eq}</i>
Cl(1)	0.5043(3)	0.3478(3)	0.1932(6)	0.0443(2)	C(9)	0.5356(1)	0.2377(1)	0.2901(2)	0.0311(5)
Cl(2)	0.4051(3)	0.1433(4)	0.0943(7)	0.0568(2)	C(10)	0.4964(1)	0.1518(1)	0.2419(2)	0.0353(6)
O(1)	0.6519(7)	0.3324(8)	0.4684(1)	0.0341(4)	C(11)	0.5334(1)	0.0545(1)	0.3068(2)	0.0377(6)
O(2)	0.4935(9)	-0.0203(1)	0.3071(2)	0.0661(6)	C(12)	0.6293(1)	0.0534(1)	0.3507(2)	0.0325(5)
N(1)	0.7941(1)	0.1413(1)	0.6665(2)	0.0537(6)	C(13)	0.6730(1)	0.1572(1)	0.4089(2)	0.0303(5)
N(2)	0.6834(1)	-0.1027(1)	0.5239(3)	0.0666(8)	C(14)	0.7418(1)	0.1491(1)	0.5532(2)	0.0365(6)
C(1)	0.6505(1)	0.3253(1)	0.6393(2)	0.0372(6)	C(15)	0.6595(1)	-0.0346(1)	0.4485(2)	0.0427(6)
C(2)	0.5964(1)	0.4043(1)	0.6958(2)	0.0466(7)	C(16)	0.6999(1)	0.1681(1)	0.2428(2)	0.0320(5)
C(3)	0.5096(1)	0.3832(1)	0.5881(2)	0.0458(7)	C(17)	0.7929(1)	0.1523(1)	0.2438(2)	0.0407(6)
C(4)	0.5099(1)	0.2716(1)	0.6339(2)	0.0402(6)	C(18)	0.7867(1)	0.1410(2)	0.0674(3)	0.0470(7)
C(5)	0.5347(1)	0.2820(2)	0.8135(3)	0.0548(8)	C(19)	0.7526(1)	0.0526(2)	0.0220(2)	0.0488(7)
C(6)	0.5866(2)	0.3592(2)	0.8504(3)	0.0589(9)	C(20)	0.7346(1)	0.0022(1)	0.1656(2)	0.0417(6)
C(7)	0.5932(1)	0.2322(1)	0.6022(2)	0.0323(5)	C(21)	0.6569(1)	0.0648(1)	0.1909(2)	0.0336(5)
C(8)	0.6101(1)	0.2381(1)	0.4351(2)	0.0297(5)	C(22)	0.8082(1)	0.0427(2)	0.2962(2)	0.0440(7)

Table V. Interatomic distances (Å) for cycloadduct (4). Standard deviations are given in parentheses.

C(1)-C(9)	1.708(2)	C(2)-C(10)	1.719(4)	O(1)-C(1)	1.493(2)	O(1)-C(8)	1.430(2)
O(2)-C(11)	1.197(2)	N(1)-C(14)	1.140(3)	N(2)-C(15)	1.131(3)	C(1)-C(2)	1.536(3)
C(1)-C(7)	1.545(3)	C(2)-C(3)	1.527(4)	C(2)-C(6)	1.516(3)	C(3)-C(4)	1.540(3)
C(4)-C(5)	1.516(3)	C(4)-C(7)	1.555(3)	C(5)-C(6)	1.326(3)	C(7)-C(8)	1.545(3)
C(8)-C(9)	1.523(4)	C(8)-C(13)	1.551(2)	C(9)-C(10)	1.331(3)	C(10)-C(11)	1.484(3)
C(11)-C(12)	1.529(3)	C(12)-C(13)	1.585(2)	C(12)-C(15)	1.594(3)	C(12)-C(21)	1.594(3)
C(13)-C(14)	1.469(4)	C(13)-C(16)	1.572(3)	C(16)-C(17)	1.555(3)	C(16)-C(21)	1.556(2)
C(17)-C(18)	1.516(3)	C(17)-C(22)	1.534(3)	C(18)-C(19)	1.323(3)	C(19)-C(19)	1.509(3)
C(20)-C(21)	1.552(3)	C(20)-C(22)	1.537(4)				

Table VI. Bond angles (deg) for cycloadduct (4). Standard deviations are given in parentheses.

C(1)-O(1)-C(8)	91.1(2)	O(1)-C(1)-C(7)	90.2(2)	O(1)-C(1)-C(2)	115.2(2)
C(2)-C(1)-C(7)	104.2(3)	C(1)-C(2)-C(6)	102.0(2)	C(1)-C(2)-C(3)	102.0(2)
C(3)-C(2)-C(6)	100.3(3)	C(2)-C(3)-C(4)	94.4(2)	C(3)-C(4)-C(7)	103.2(3)
C(3)-C(4)-C(5)	99.2(2)	C(5)-C(4)-C(7)	100.9(3)	C(4)-C(5)-C(6)	108.1(2)
C(2)-C(6)-C(5)	107.4(2)	C(1)-C(7)-C(4)	102.2(2)	C(4)-C(7)-C(8)	121.4(2)
C(1)-C(7)-C(8)	85.0(2)	O(1)-C(8)-C(7)	92.6(2)	C(7)-C(8)-C(13)	112.7(2)
C(7)-C(8)-C(9)	118.7(4)	O(1)-C(8)-C(13)	109.6(3)	C(17)-C(22)-C(20)	94.3(2)
O(1)-C(8)-C(9)	114.7(1)	C(9)-C(8)-C(13)	107.8(2)	Cl(1)-C(9)-C(8)	119.1(1)
C(8)-C(9)-C(10)	119.3(2)	Cl(1)-C(9)-C(10)	121.6(2)	Cl(2)-C(10)-C(9)	123.8(2)
C(9)-C(10)-C(11)	120.9(3)	Cl(2)-C(10)-C(11)	115.2(2)	C(8)-C(9)-C(10)	101.3(5)
O(2)-C(11)-C(10)	123.7(3)	C(10)-C(11)-C(12)	113.8(2)	O(2)-C(12)-C(21)	108.0(3)
C(11)-C(12)-C(15)	109.4(3)	C(11)-C(12)-C(13)	115.4(2)	C(15)-C(12)-C(21)	116.6(2)
C(13)-C(12)-C(21)	88.8(2)	C(13)-C(12)-C(21)	117.1(2)	C(8)-C(13)-C(12)	112.8(2)
C(12)-C(13)-C(16)	90.2(2)	C(12)-C(13)-C(14)	113.6(1)	C(8)-C(13)-C(16)	114.4(2)
C(8)-C(13)-C(14)	109.1(2)	C(14)-C(13)-C(16)	115.9(4)	N(1)-C(14)-C(13)	178.4(3)
N(2)-C(15)-C(12)	179.4(6)	C(13)-C(16)-C(21)	90.6(2)	C(13)-C(16)-C(17)	120.4(2)
C(17)-C(16)-C(21)	102.5(2)	C(16)-C(17)-C(22)	102.2(4)	C(16)-C(17)-C(18)	102.6(4)
C(18)-C(17)-C(22)	99.7(2)	C(17)-C(18)-C(19)	107.9(2)	C(18)-C(19)-C(20)	107.9(2)
C(19)-C(20)-C(22)	99.9(2)	C(19)-C(20)-C(21)	101.7(2)	C(21)-C(20)-C(22)	102.5(2)
C(16)-C(21)-C(20)	103.3(3)	C(12)-C(21)-C(20)	120.3(2)	C(12)-C(21)-C(16)	90.4(2)

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