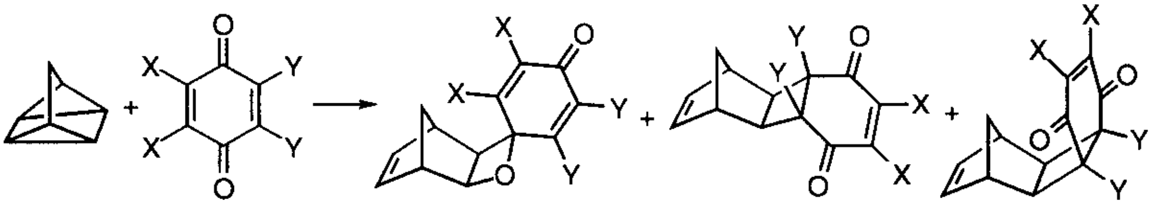
THE REACTION OF QUADRICYCLANE WITH *p*-ANILS

Fabrizio Fabris,[†] Ottorino De Lucchi,[†*] Giovanni Valle,[‡1] and Sergio Cossu[†]

[†]Dipartimento di Chimica, Università di Venezia, Dorsoduro 2137,
I-30123 Venezia, Italy
[‡]C.N.R., Centro Studi Biopolimeri, via Marzolo 1, I-35131 Padova, Italy

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 C_2-symmetric chiral ketones[2] 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 complex[4] 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.



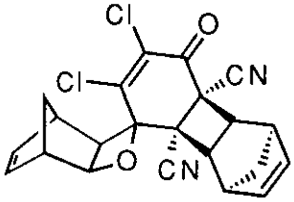
Q **A** **1** **2** **3**

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.

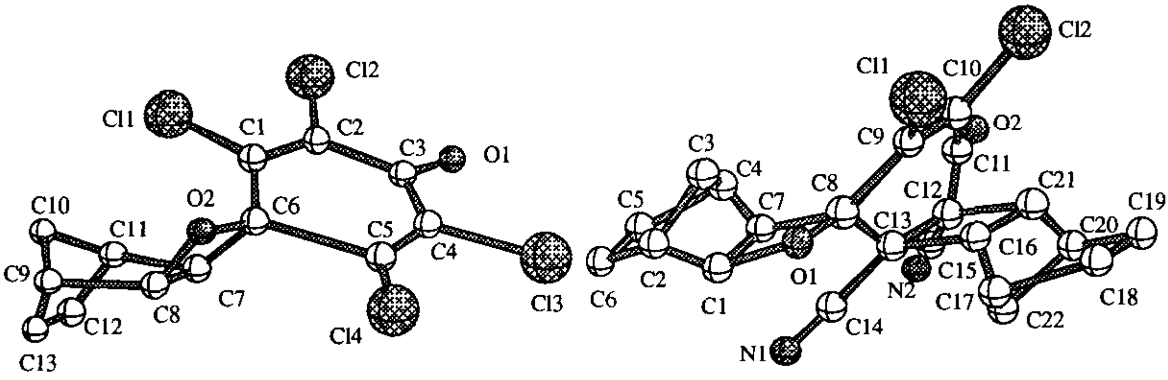
p-Quinone	Solvent	Temp. (°C)	1	2	3
X = Y = H[2,3]	neat	90	-	100	-
X = Y = F	CH_2Cl_2	0	75	15	10
X = Y = Cl	CH_2Cl_2	25	80	15	5
X = Y = Br	CH_2Cl_2	25	40	10	-
X = Cl; Y = CN	CH_2Cl_2	40	-	50	traces

Comparatively to *p*-chloroanil, the reaction of the tetrafluoro derivative occurs more rapidly and cooling of the reaction mixture to 0 °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.



4

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

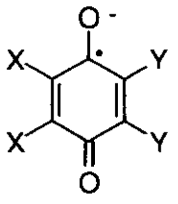


1 **4**

Figure 1. Perspective representation of (**1**) (X = Y = 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 separatly 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 benzoquinone[8] and of **Q**$^{+\cdot}$ as that derived from quadricyclane. The latter radical cation **Q**$^{+\cdot}$ rearranges rapidly[5] 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 photoexited *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 exitation of other sensitizers (1-cyanonaphthalene, for example).[5,8]



A$^{-\cdot}$

N$^{+\cdot}$

Q$^{+\cdot}$

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*-benzoquinone[10] 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 products[13] 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 ^{13}C 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 chromatograpy 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 untill 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 ($CDCl_3$) 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); ^{13}C nmr ($CDCl_3$) 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 $C_{13}H_8O_2Cl_4$: 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. $C_{13}H_8O_2Cl_4$ crystallized in the monoclinic system, space group $P2_{1/n}$, $a = 8.030(1)$, $b = 16.768(2)$, $c = 10.467(2)$ Å, $\beta = 108.2(1)°$, $V = 1339$ Å^3, $Z = 4$, $D_c = 1.69$ g cm^{-3}. 3429 Reflections were collected on a four-circle Philips PW 1100 diffractometer up to $\theta = 28°$, θ-2θ = 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 ($Å^2 x 10^3$) parameters for cycloadduct (**1**) (X = Y = 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*	*Ueq*	Atom	*x*	*y*	*z*	*Ueq*
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 (Å) for cycloadduct (**1**) (X = Y = 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 = 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 = Cl): (15 %). mp 224 °C (decomp.) (from dichloromethane/ hexane). ^{1}H 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 $C_{13}H_8O_2Cl_4$: C, 46.2; H, 2.4. Found: C, 46.4; H, 2.4.

3 (X = Y = Cl): (5 %). mp 147-148 °C (from dichloromethane/ hexane). ^{1}H 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 $C_{13}H_8O_2Cl_4$: 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 $C_{13}H_8O_2F_4$: 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 $C_{13}H_8O_2F_4$ (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 (1H, 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 $C_{13}H_8O_2Br_4$: 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 $C_{13}H_8O_2Br_4$: 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) untill 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 ($CHCl_3$/*n*-hexane) (decomp.). ^1H Nmr (acetone-d_6) 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); ^{13}C nmr (acetone-d_6) 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 $C_{15}H_8N_2O_2Cl_2$: 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 ($CHCl_3$/ ethyl acetate). ^1H Nmr ($CDCl_3$) 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); ^{13}C nmr ($CDCl_3$) 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 $C_{22}H_{16}N_2O_2Cl_2$: 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. $C_{22}H_{16}O_2Cl_2N_2$ crystallized in the monoclinic system, space group $P2_{1/n}$ a = 16.461(2), b = 13.344(2), c = 8.681(2) Å, β = 104.4(2)°, V = 1847 Å^3, 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 '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 3090 observed reflections [$F > 5\sigma(F)$] 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 (Å^{2}x10^3) 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	*x*	*y*	*z*	*Ueq*	Atom	*x*	*y*	*z*	*Ueq*
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.

Cl(1)-C(9)	1.708(2)	Cl(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)

ACKNOWLEDGMENT

The authors wish to thank Mr. A. Canu of the "Dipartimento di Chimica dell'Università di Sassari" for the microanalytical determinations.

REFERENCES AND NOTES

1. Author to whom inquires concerning the X-ray structure analysis should be directed.
2. O. De Lucchi and F. Fabris, *Synlett*, 1993, 275.
3. G. Kaupp and H. Prinzbach, *Chem. Ber.*, 1971, **104**, 182.
4. I. Tabushi and K. Yamamura, *Tetrahedron*, 1975, **31**, 1827. G. Jones II and W. G. Becker, *Chem. Phys. Lett.*, 1982, **85**, 271.
5. H. D. Roth, M. L. Manion Schilling, and G. Jones, II, *J. Am. Chem. Soc.*, 1981, **103**, 1246. H. D. Roth and M. L. Manion Schilling, *Ibid.*, 1981, **103**, 7210. G. Jones II, S. H. Chiang, W. G. Becker, and J. A. Welch, *J. Phys. Chem.*, 1982, **86**, 2805.
6. When this work was in progress we became aware that the same reaction was observed by Hirao *et al.* (Ref. 7). Our data are generally in agreement and complement those reported.

7. K. Hirao, T. Yokozawa, A. Yamashita, and T. Watanabe, *Heterocycles*, 1992, **34**, 1503.
8. H D. Roth and M. L. Manion Schilling, *J. Am. Chem. Soc.*, 1980, **102**, 4303.
9. P. G. Gassman and K. D. Olson, *Tetrahedron Lett.*, 1983, **24**, 19.
10. E. A. Fehnel and F. C. Brokaw, *J. Org. Chem.*, 1980, **45**, 578.
11. A. J. G. Barwise, A. A. Gorman, R. L. Leyland, C. T. Parekh, and P. G. Smith, *Tetrahedron,* 1980, **36,** 397.
12. M. Papadopoulos, R. Jost, and G. Jenner, *J. Chem. Soc., Chem. Commun.,* 1983, 221.
13. K. Hirao, T. Yokozawa, K. Hasebe, A. Yamashita, T. Watanabe, and T. Hamada, *Tetrahedron Lett.,* 1992, **33**, 6971.
14. W. Friedrichsen, E. Büldt, and R. Schmidt,*Tetrahedron Lett.,* 1975, 1137.
15. G. M. Sheldrick, In *Crystallographic Computing 3*, G. M. Sheldrick, C. Krüger, and R. Goddard, Eds.; Oxford University Press, 1985, pp. 175-189.

Received, 28th June, 1993