Structure and Spectroscopic Properties of *p*-Benzoquinone Diazides

Wolfram Sander*[a], Götz Bucher[a], Peter Komnick[a], Jens Morawietz[a], Peter Bubenitschek[a], Peter G. Jones[b] and Axel Chrapkowski[b]

Institut für Organische Chemie der Technischen Universität Braunschweig[a],
Hagenring 30, D-38106 Braunschweig

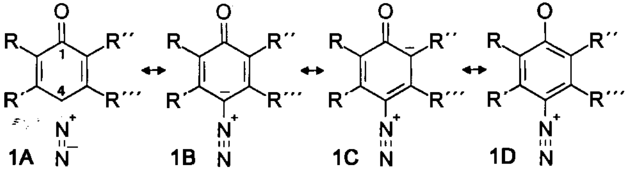
Institut für Anorganische und Analytische Chemie der Technischen Universität Braunschweig[b],
Hagenring 30, D-38106 Braunschweig

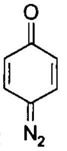
Received March 25, 1993

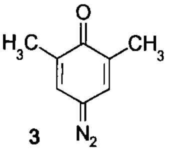
Key Words: Quinone diazides / Matrix isolation / Electronic structure

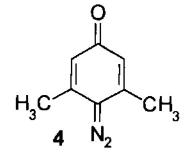
A series of *p*-benzoquinone diazides were investigated by ^{13}C-NMR and IR spectroscopy as well as by semiempirical and ab initio calculations. In addition, X-ray structure analyses of the parent compound and three derivatives were performed. The electronic structure and effects of substituents can be described in terms of diazoketo and diazonium phenolate resonance structures. While alkyl groups as substituents have only a minor influence on quinone diazides, electron-withdrawing substituents lead to a larger participation of the aromatic diazonium phenolate structure. Benzoannellation, on the other hand, leads to a decrease of the interaction between the keto and diazo functional group and to properties more reminiscent of "ordinary" ketones and diazo compounds.

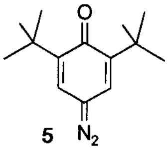
p-Benzoquinone diazides **1** (derivatives of 4-diazo-2,5-cyclohexadien-1-one) are molecules with an unusual electronic structure that have found use as carbene precursors in synthetic organic chemistry, as stabilizers for polymers, and for the development of photolithographic materials[1]. The electronic structure of these species can be described in terms of diazo-keto and diazonium phenolate resonance structures **1A**–**1D**. In addition, diradicaloid resonance structures can be formulated, as suggested by Walch and Goddard[2].

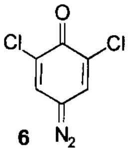


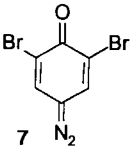

2

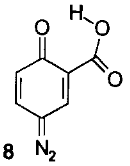

3

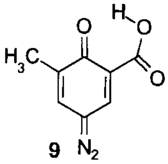

4

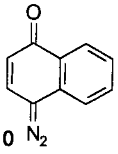

5

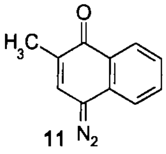

6

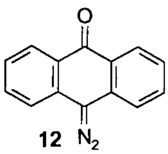

7


8


9


10


11


12

The cyclohexadienone system is well suited for a systematic study of substituent effects, because this rigid cyclic system is easily modified with a variety of substituents at C(2), C(3), C(5), and C(6). Thus, both the electronic and steric properties at C(4) can be modified substantially. Experimental values which afford an insight into the electronic structure of quinone diazides **1** are (i) the bond lengths of the C(4)–N(1), N(1)–N(2), and C(1)–O bonds as determined by X-ray analysis, (ii) the ^{13}C-NMR classical shifts of C(1) and C(4), and (iii) the frequencies of the $\nu_{\mathrm{C=O}}$ and $\nu_{\mathrm{N=N}}$ vibrations determined by IR spectroscopy.

In this paper we describe the spectroscopic properties of quinone diazides **2**–**12** with substituents ranging from electron-donating alkyl groups, as in **3**–**5**, to electron-withdrawing substituents, as in **6**–**9**. The effect of benzoannellation was studied with **10**–**12**. Infrared data of **2**–**12**, matrix-isolated in argon, and ^{13}C-NMR data in solution are reported. Matrix isolation is helpful for the investigation of properties of highly polar compounds such as **1**, because intermolecular interactions and the formation of dimers or higher aggregates are largely avoided. The photochemistry[3] and oxidation[4] of matrix-isolated quinone diazides **2**–**4**, **6**–**8**, **10**, and **11** have been described elsewhere. X-ray structures of **2**, **5**, **8**, and **12** have been determined and are compared to the structure of **6**, which was previously the only experimentally known structure of a *p*-benzoquinone diazide (although of limited precision; room-temperature photographic data from several crystals, appreciable crystal decomposition)[7].

Results and Discussion

Crystal Structures

The ring system, diazo, and carbonyl group of quinone diazides **2**, **5**, **8**, and **12** form planar system with only small deviations from planarity (Figures 1–4). The C(6)–C(1)–C(2) bond angle is always significantly smaller (116–119°) than the C(3)–C(4)–C(5) bond angle (122–124°) (Table 1). The C(4)–N(1) and N(1)–N(2) distances are diagnostic of the charge distribution in these molecules. A large contribution of resonance structure **1A** should lead to short C(4)–N(1) and C(1)–O distances, while increasing participation of the aromatic resonance structure **1D** should result in lengthening of the C(1)–O and the C(4)–N(1) bond and in shortening of the N(1)–N(2) bond. A short N(1)–N(2) and long C(4)–N(1) bond should also result from a major contribution of resonance structures **1B** and **1C**, but in this case the C(1)–O bond is expected to exhibit more double bond than single bond character.

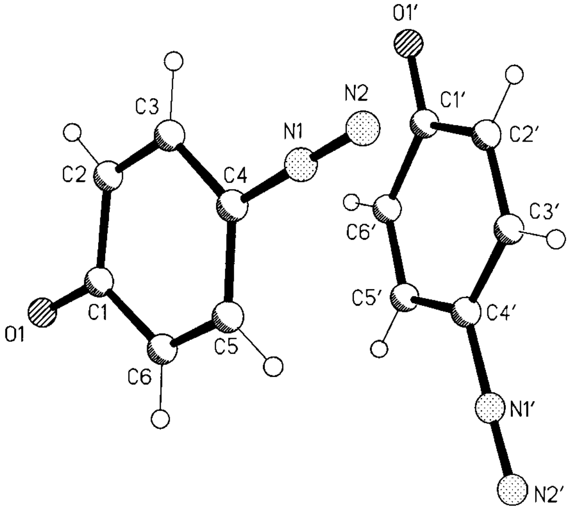


Figure 1. Molecular structure of 4-diazo-2,5-cyclohexadien-1-one (**2**). The orientation of the two independent molecules in the unit cell is shown

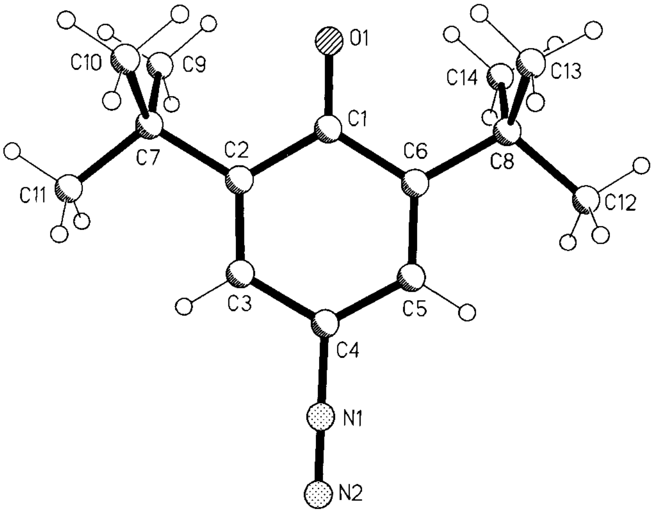


Figure 2. Molecular structure of 2,6-di-*tert*-butyl-4-diazo-2,5-cyclohexadien-1-one (**5**)

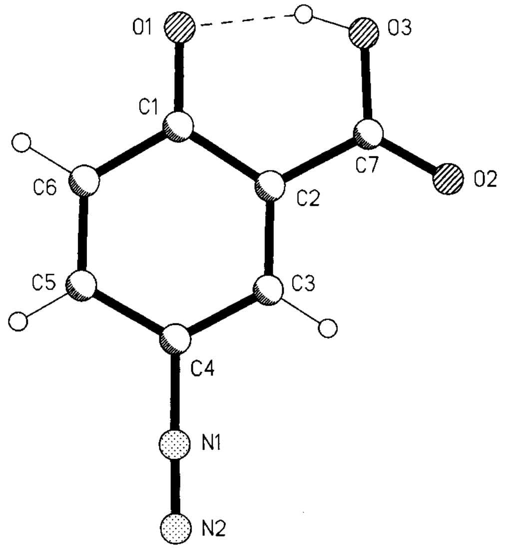


Figure 3. Molecular structure of 3-diazo-6-oxo-1,4-cyclohexadiene-1-carboxylic acid (**8**)

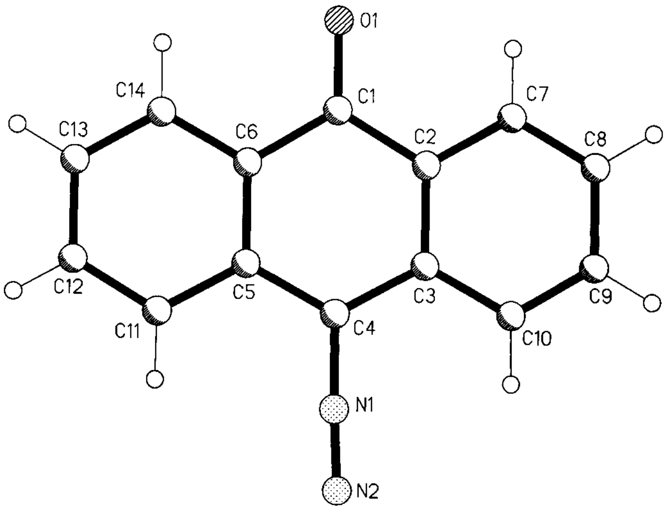
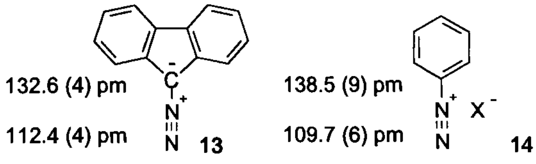


Figure 4. Molecular structure of 10-diazo-9(10*H*)-anthracenone (9-diazo-10-anthrone) (**12**). Only one of four independent molecules is shown

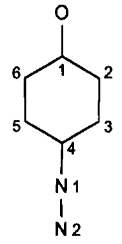
For 9-diazofluorene (**13**) a C–N distance of 132.6 and a N–N distance of 112.4 pm was reported[5], the corresponding values for benzenediazonium chloride (**14**, X = Cl) are 138.5 and 109.7 pm[6]. These two compounds can be taken as examples with partial or complete positive charge, re-



spectively, at the diazo functional group. In both molecules the N—N distance is much closer to that expected for a triple bond (109.75 pm in N_2) than for a double bond (approximately 124 pm in azo compounds).

The C(4)—N(1) and N(1)—N(2) distances of the quinone diazides in Table 1 span almost the entire range between **13** and **14**, with the parent compound **2** holding an intermediate position. Generally a long C(4)—N(1) distance correlates with a short N(1)—N(2) distance. Diazoanthrone **12** exhibits a slightly shorter C—N distance (132.0 pm) and longer N—N distance (113.3 pm) than diazofluorene, which indicates that in this molecule the carbonyl group does not substantially interact with the diazo group. The diazo group is described best in terms of resonance structures **1A** and **1B**.

Table 1. Structural data of quinone diazides **2**, **5**, **6**, **8**, and **12**



Parameter[a]	**2**[b]	**5**	**6**[c]	**8**	**12**[d]
C(1)-C(2)	144.4 (2)[e]	148.1 (7)[e]	144.8 (18)[e]	145.0 (3)	146.7 (6)[e]
C(1)-C(6)				142.7 (3)	
C(2)-C(3)	134.8 (2)[f]	135.1 (7)[f]	136.5 (18)[f]	136.3 (3)	139.9 (6)[f]
C(5)-C(6)				135.8 (3)	
C(3)-C(4)	141.4 (2)[g]	142.4 (8)[g]	141.7 (18)[g]	139.8 (3)	144.1 (6)[g]
C(4)-C(5)				141.5 (3)	
C(1)-O	125.0 (2)	123.4 (6)	122.1 (16)	128.5 (3)	123.9 (5)
C(4)-N(1)	134.5 (2)	133.2 (7)	136.8 (16)	136.8 (3)	132.0 (5)
N(1)-N(2)	111.5 (2)	111.4 (6)	110.0 (15)	110.2 (3)	113.3 (5)
C(6)-C(1)-C(2)	116.2 (2)	119.0 (6)	114.0 (12)	117.7 (2)	118.2 (4)
C(3)-C(4)-C(5)	122.1 (2)	121.8 (6)	123.9 (12)	122.8 (2)	123.5 (4)

[a] Bond parameters determined by X-ray crystallography, bond lengths in pm and bond angles in degrees (standard deviation). — [b] Average of two independent molecules. — [c] Ref.[7], average of two independent molecules. — [d] Average of four independent molecules. — [e] Average over the equivalent bonds C(1)—C(2) and C(1)—C(6). — [f] Average over the equivalent bonds C(2)—C(3) and C(5)—C(6). — [g] Average over the equivalent bonds C(3)—C(4) and C(4)—C(5).

While the *tert*-butyl groups in **5** lead to a small but significant shortening of the C(4)—N(1) bond, the N(1)—N(2) distances in **5** and **2** are almost identical (Table 1). Carboxylic acid **8** and the dichloro derivative **6**[7], on the other hand, have long C(4)—N(1) (136.8 pm) and short N(1)—N(2) distances (110.2 and 110.0 pm, respectively). These values are closer to those expected for a diazonium rather than a diazo moiety, indicating the importance of the aromatic resonance structure **1D** in quinone diazides bearing electronegative substituents.

The C—O bonds of quinonediazides **2**, **5**, **8**, and **12** (Table 1) are considerably longer than those of carbonyl compounds such as 9-fluorenone (122.0 pm)[8] or quinones (2,6-dichloro-1,4-benzoquinone: C(1)—O 121.3 and C(4)—O 121.7 pm)[9]. The only exception is the dichloro derivative **6** with a C(1)—O bond length of only 122.1 pm[7]. However, the standard deviation from this value is rather high, and the data for **6** should be interpreted with some caution. Long C(1)—O bonds require substantial contribution of resonance structures **1B**—**1D**. Inspection of the data in Table 1 reveals that long C(4)—N(1) distances correspond to long C(1)—O distances, again in agreement with qualitative theory.

Remarkable is the very long C(1)—O(1) distance (128.5 pm) of **8**, which indicates a bond order of substantially less than two resulting from the strong intramolecular O—H – O hydrogen bond in this molecule. The strong hydrogen bond is also reflected in the very short O(1)—O(3) distance of only 247.5 pm (Figure 3). This distance is shorter than the O—O distance of malonaldehyde in the gas phase (255.3 pm)[10] and in the order of the shortest O—H – O bonds known[11].

The structures of quinone diazides **1** have been calculated by using ab initio methods[22,23] (Table 4) and the semiempirical AM1 method[12] (Table 5). The bond lengths in **2** are only poorly reproduced by both ab initio and semiempirical methods using spin-restricted Hartree-Fock (RHF) wave functions. The C(1)—O and C(4)—N(1) bonds are consistently calculated too short and the C(1)—C(2) and C(3)—C(4) bonds too long. At the RHF level these theoretical methods underestimate the aromatic resonance structure **1D**. Using unrestricted Hartree-Fock (UHF) AM1 calculations, we have found that the heat of formation of **2** drops by 3.75 kcal/mol, which indicates a partial diradical character[13] of the wave function. The calculated bond lengths of **2** are now closer to the experimental values (Table 4). However, a problem is now the N(1)—N(2) distance which is calculated too long. Similar observations were made by using AM1 with a 3 × 3 configuration interaction. Calculations on **8** and **9** with a variety of semiempirical methods (AM1, MNDO, PM3) largely underestimate the strength of the O—H – O hydrogen bridge.

^{13}C-NMR Spectra

Roberts et al. reported NMR data of a series of diazo and diazonium compounds[14,15]. The ^{13}C-NMR chemical shift of diazomethane is $\delta = 23.3$, reflecting a partial negative charge at C(4). For 9-diazofluorene (**13**) a value of 63.2 ($CDCl_3$) and for diphenyldiazomethane 62.3 ($CDCl_3$) was observed, revealing a partial delocalization of the negative charge into the aromatic system. Quinone diazide **2**, with the strongly electron-accepting cyclohexadienone moiety, exhibits chemical shifts of $\delta = 73.6$ in $CDCl_3$ and 75.2 in $[D_6]$DMSO (Table 2). This is in accordance with some contribution of resonance structure **1D** to the electronic structure of **2**. For *p*-hydroxybenzenediazonium tetrafluoroborate (**14**, *p*-OH instead of *p*-H, $X = BF_4$) the resonance of C(4) is shifted downfield to $\delta = 102.1$ ($CHCl_3$ containing 18-crown-6 as solvent), which is the value expected for "pure" structure **1D**. A chemical shift of $\delta = 101.7$ was observed for **2** in CF_3CO_2D

Table 2. ^{13}C-NMR data of quinone diazides **2**–**12**. δ values, downfield from TMS

	Solvent	C(4)	C(1)
2	$CDCl_3$	73.6	182.2
	$[D_6]$-DMSO	75.2	180.8
	CF_3COOD	101.7	173.4
3	$CDCl_3$	-	182.0
	$[D_6]$-DMSO	72.6	180.5
4	$[D_6]$-Acetone	77.8	181.8
5	$CDCl_3$	71.0	181.1
6	$[D_6]$-DMSO	78.4	169.0
7	$[D_6]$-DMSO	80.2	159.2
8	$[D_6]$-DMSO	87.0	165.7
	CF_3COOD	103.6	172.4
9	$[D_6]$-DMSO	85.9	166.1
	CF_3COOD	102.5	172.9
10	$CDCl_3$	74.9	181.0
11	$CDCl_3$	67.5	181.0
12	$CDCl_3$	64.5	179.9

(Table 2), which clearly shows complete protonation at the oxygen atom in this solvent.

The ^{13}C-NMR chemical shift of the carbonyl carbon C(1) of **2** exhibits just the opposite solvent effect: an upfield shift from δ = 182.2 to 180.0 and 173.4 in $CDCl_3$, $[D_6]$DMSO, and CF_3CO_2D, respectively, with increasing ability of the solvent to stabilize a negative charge at the oxygen atom. The chemical shifts ($CDCl_3$) of C(1) in *p*-benzoquinone are δ = 187.0[16] and in phenol 154.9. The latter resonance is shifted downfield by electron-accepting groups in the 4-position (e.g. δ = 161.8 in 4-nitrophenol). Thus, the transition of the quinoid to the aromatic structure on changing the solvent to CF_3CO_2D is also reflected in the chemical shift of C(1).

Substituent effects on ^{13}C-NMR shifts of quinone diazides can be seen in Table 2. The chemical shift of C(4) in **12** is very close to that of the diazo carbon in diazofluorene **13**. Obviously, the electronic coupling between the carbonyl and diazo group in **12** is much weaker than in **2**. For **10** no such effect is observed. The chemical shift of the carbonyl carbon atom C(1) in **2** is not much affected on benzoannellation with one (**10** and **11**) or two (**12**) benzo groups and lies at considerably higher field than the carbonyl carbon resonances of benzophenone (δ = 196.4 in $CDCl_3$) or fluorenone (193.7 in $CDCl_3$).

Whereas alkyl groups at C(2) and C(6) (compounds **3** and **5**) or methyl groups at C(3) and C(5) (compound **4**) show only a minor influence on the ^{13}C-NMR resonances of C(1) and C(4), electron-accepting groups at C(2) or C(6) result in significant downfield shifts of the C(4) and upfield shifts of the C(1) signals (compounds **6**–**9**). The largest effects are observed with carboxylic acids **8** and **9**. The C(4) resonance of **8** at δ = 87.0 is almost exactly halfway between **2** and **14**, and the C(1) resonance is close to that of phenol. The influence of one carboxy group in **8** or **9** is much larger than that of two chlorine substituents in **6**, which reflects the strong intramolecular hydrogen bond and substantial charge transfer from the diazo to the C(1)–O carbonyl group. The additional methyl group in **9** has only a minor influence on the C(1) and C(4) resonances. In CF_3CO_2D as solvent, **8** and **9** are completely protonated and benzenediazonium ions are formed. The chemical shifts of C(1) and C(4) are now close to that of the corresponding carbons of **2** in CF_3CO_2D, indicating only small effects of the carboxy group on the benzenediazonium ion. This also reveals that the large effect of the carboxy group in **8** and **9** in $[D_6]$-DMSO is almost entirely caused by the hydrogen bond. The ^{1}H-NMR resonance of the proton in the hydrogen bond is as expected at very low field: δ = 16.05 and 13.53 for **8** and **9**, respectively, in $[D_6]$DMSO.

Matrix IR Spectra

Quinone diazides **2**–**12** were matrix-isolated in argon at 10 K and characterized by IR spectroscopy (Table 3 and 4). To assign IR absorptions of **2**, the tetradeuterated and ^{18}O-labelled isotopomers $[D_4]$-**2** and $[^{18}O]$-**2** have been investigated (Table 6, Figure 5). In addition, IR spectra of these isotopomers were calculated with ab initio methods by using the 6-31G(d,p) basis set (Table 6, Figure 6). The calculations reproduce the experimental band positions, intensities, and isotopic shifts reasonably well, and thus were used as a basis of the assignment of fundamental vibrations of **2**.

There are two characteristic vibrations of quinone diazides **1** which can be easily identified: the C=O str. vibration at 1575–1657 cm^{-1} and the N≡N str. vibration at 2059–2114 cm^{-1} (for a discussion of the IR spectra of **1** see also ref.[1]). These absorptions are generally the most intense absorptions in **1**. The range of $\nu_{N\equiv N}$ expected is between $\nu_{N\equiv N}$ of diazo compounds such as **13** (in argon at 10 K two bands at 2074 and 2096 cm^{-1} were observed)[17] and

Table 3. $\nu_{C(1)=O}$ and $\nu_{N\equiv N}$ vibrations of quinone diazides **2**–**12**, matrix-isolated in argon at 10 K

	$\nu_{C(1)=O}$, [cm^{-1}]	$\nu_{C(1)=O}$, [cm^{-1}] Quinone[a]	Δ[b]	$\nu_{N\equiv N}$, [cm^{-1}]
2	1624.7	1672 (1666)[c]	47	2076.0
$[D_4]$-**2**	1616.5	(1660)[c]	(43.5)	2079.4
$[^{18}O]$-**2**	1605.0	(1634)[c]	(29)	2072.6
3	1618.0	1658.0	40	2064.4
4	1634.4	1666.2	31.8	2070.7
5	1596.3	1663.3	67	2066.4
6	1579.9	1702.4	122.5	2076.5
7	1575.6	1695.1	119.5	2088.0
8	1595.8	-[d]	-	2113.6
9	1605.4	-[d]	-	2104.4
10	1643.5	1682.1	38.6	2071.7
11	1635.8	1679.2	43.4	2062.0
12	1657.5	1684.5	27	2059.6

[a] Quinone corresponding to quinone diazide. – [b] Difference $\nu_{C(1)=O}$ (quinone) – $\nu_{C(1)=O}$ (quinone diazide). – [c] Ref.[19b], gas phase. – [d] The quinone is unstable, and IR data are not available.

Table 4. Some structural parameters of quinone diazide **2**, calculated according to ab initio and semiempirical methods

Parameter[a]	X-Ray[b]	3-21G[c]	6-31-G(d,p)[d]	RHF[e] AM1	UHF[f] AM1	CI[g] AM1
C(1)-O	125.0 (2)	122.2	123.4	124.1	124.6	124.2
C(1)-C(2)[h]	144.5 (2)	147.0	146.8	146.9	146.5	146.6
C(2)-C(3)[i]	134.8 (2)	133.0	134.1	134.7	136.2	135.2
C(3)-C(4)[k]	141.4 (2)	143.9	144.1	145.2	144.4	144.5
C(4)-N(1)	134.5 (2)	130.2	131.0	133.7	134.7	133.9
N(1)-N(2)	111.5 (2)	111.6	111.9	112.8	113.9	113.6
C(6)-C(1)-C(2)	116.2 (2)		116.9			
C(3)-C(4)-C(5)	122.1 (2)		120.2			

[a] Bond lengths in pm and bond angles in degrees (standard deviation). C_{2v} symmetry was assumed. — [b] See Table 1. — [c] Ab initio calculation, 3-21G basis set, RHF. — [d] Ab initio calculation, 6-31G(d,p) basis set, RHF. — [e] AM1 calculation, RHF. — [f] AM1 calculation, UHF. — [g] AM1 calculation, using the BIRADICAL keyword, 3 × 3 CI. — [h] Equivalent to C(1)—C(6). — [i] Equivalent to C(5)—C(6). — [k] Equivalent to C(4)—C(5).

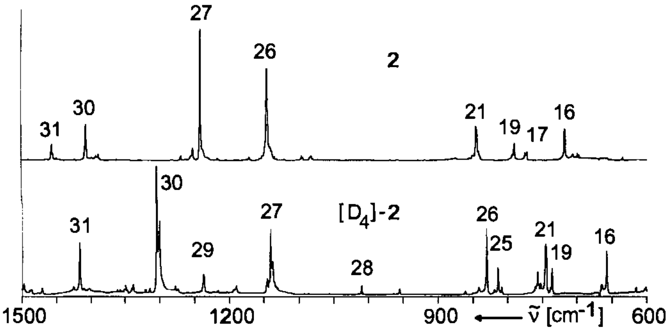


Figure 5. IR-spectra of quinone diazide **2** (top) and [D$_4$]-**2** (bottom), matrix-isolated in argon at 10 K. Assignment of vibrations according to Table 6

$\nu_{N\equiv N}$ of benzenediazonium salts **14** (X = BF$_4$, 2280 cm^{-1}, Nujol mull)[18]. For *p*-hydroxybenzenediazonium chloride an N≡N str. absorption of 2240 cm^{-1} was reported[18].

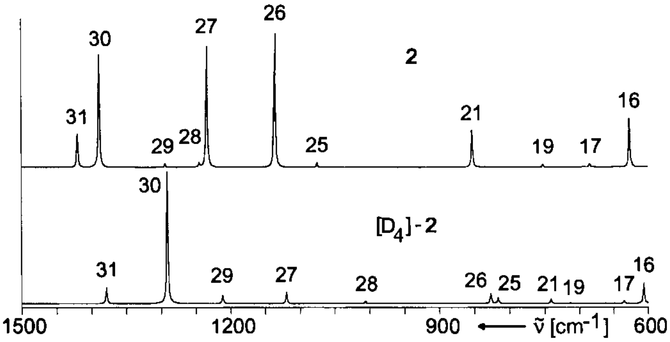


Fig. 6. IR-spectra of quinone diazide **2** (top) and [D$_4$]-**2** (bottom), ab initio calculation [RHF/6-31G(d,p) basis set, scaled with 0.9]. Assignment of vibrations according to Table 6

A problem in assigning these vibrations arises from the frequently observed splitting into multiple components. The splitting is almost unaffected by changing the matrix (e.g. using xenon instead of argon for **2**), but is greatly affected by isotopic substitution. The patterns of bands observed in the N≡N and C=O str. regions are quite different for **2**, [D$_4$]-**2**, and [^{18}O]-**2**. Thus, the splitting is presumably not caused by matrix site effects, but rather by Fermi resonance. Fermi resonance has also been shown to cause the splitting of $\nu_{C=O}$ in *p*-benzoquinone[19]. Because normal coordination analysis of large molecules such as **1** is very difficult, if not impossible, and requires extensive isotopic labelling, the exact positions of fundamental vibrations have not been determined. For the qualitative discussion of substituent effects the most intense vibrations in the region of interest have been used.

On tetradeuteration $\nu_{N\equiv N}$ is slightly blue-shifted, while ^{18}O labelling has no influence on the position of this band (Table 6). The absorptions in the region 1600–1650 cm^{-1}, on the other hand, are sensitive to both deuteration and ^{18}O labelling. These absorptions are assigned to two vibrations with large contributions of C=O and C=C stretching. As a consequence, the isotopic shifts on ^{18}O labelling are smaller than expected for a C=O str. vibration. For a diatomic C–O oscillator at 1650 cm^{-1} a red shift of 40 cm^{-1} is calculated,

Table 5. Some structural parameters of quinone diazides **2**–**12**, calculated according to the semiempirical AM1 method

	C(4)-N(1)[a]	N(1)-N(2)[a]	C(1)-O[a]	C(4)[b]	N(1)[b]	N(2)[b]	C(1)[b]	O[b]	ΔH_f[c]
2	133.7	112.8	124.4	-0.216	0.166	0.040	0.282	-0.311	60.88
3	133.7	112.8	124.1	-0.202	0.162	0.034	0.290	-0.312	46.56
4	133.6	112.8	124.2	-0.196	0.170	0.032	0.288	-0.318	49.26
5	133.7	112.8	124.3	-0.206	0.162	0.032	0.300	-0.322	27.98
6	134.1	112.6	123.6	-0.204	0.170	0.067	0.302	-0.260	51.82
7	134.2	112.5	123.6	-0.215	0.173	0.076	0.309	-0.261	76.15
8	134.6	112.4	124.5	-0.226	0.180	0.095	0.305	-0.339	-26.73
9	134.6	112.4	124.5	-0.219	0.178	0.092	0.309	-0.340	-33.85
10	133.6	112.9	124.2	-0.201	0.163	0.030	0.299	-0.311	73.32
11	133.6	112.9	124.2	-0.194	0.160	0.027	0.302	-0.312	66.09
12	133.6	113.0	124.3	-0.183	0.159	0.020	0.313	-0.313	86.00

[a] Bond distance in pm. — [b] Atomic charge in atomic units. — [c] Heat of formation in kcal/mol.

Table 6. IR spectroscopic data of quinone diazide **2**, matrix-isolated in argon at 10 K and calculated by ab inito methods with an HF/6-31G(d,p) basis

		Ar matrix				RHF/6-31G(d,p)				
Nr.	Sym.	ν [cm^{-1}]	I[a]	Δ[b]	Δ[c]	ν [cm^{-1}][d]	I[a]	Δ[b]	Δ[c]	Assignment[e]
33	a1	-	-	-	-	3032.3	0.1	0.746	1.000	C-H str.
32	b1	-	-	-	-	3030.6	0.3	0.745	1	C-H str.
31	b1	-	-	-	-	2995.1	0.01	0.741	1	C-H str.
30	a1	-	-	-	-	2994.7	0.4	0.741	1	C-H str.
29	-	2085.1	61	-	-	-	-	-	-	-
	-	2078.2	87	-	-	-	-	-	-	-
	a1	2075.8	100	1.001	1.0	2008.8	100	0.999	1.000	N≡N str.
28[f]	a1	1635.6	83	0.997	1.0	1612.1	66.2	0.991	0.995	C=O, C=C str.
		1628.2	55	0.993	0.994	-	-	-	-	
27[f]	a1	1626.4	32	0.982	0.991	1584.1	4.3	0.977	0.990	C=O, C=C str.
		1617.1	17	-	-	-	-	-	-	
26	b1	-	-	-	-	1560.1	0.1	0.979	1.0	
25	b1	1455.4	5	0.973	0.999	1420.5	2.6	0.971	1.0	
24	a1	1406.4	11	0.927	0.998	1389.3	8.9	0.929	0.997	
23	b1	1269.4	1	0.974	0.998	1294.2	0.3	0.936	1.0	
22	b1	1252.1	4	0.806	1	1245.0	0.3	0.809	0.999	
21	a1	1241.2	41	0.918	1.0	1234.3	9.6	0.907	1.0	
20	a1	1145.3	30	0.725	1.0	1136.0	10.6	0.738	0.999	
19	b1	1095.4	1	0.743	1.0	1074.7	0.4	0.750	1.0	
18	a2	-	-	-	-	980.1	0	0.800	1	
17	b2	-	-	-	-	967.6	0.03	0.844	1.0	
16	a1	-	-	-	-	933.1	0.04	0.886	0.999	
15	b2	845.6	11	0.882	0.997	853.4	3.0	0.869	0.999	
14	a2	-	-	-	-	765.5	0	0.777	1	
13	a1	790.7	6	0.931	0.997	751.8	0.2	0.950	0.992	
13	b2	-	-	-	-	692.2	0.1	0.876	0.999	
13	a1	772.4	3	0.861	0.997	684.8	0.3	0.928	0.993	
10	b1	717.7	10	0.916	0.993	626.4	3.9	0.970	0.998	

[a] Relative intensity. — [b] Ratio of isotopic frequencies ν^i/ν for [D$_4$]-**2** and **2**. — [c] Ratio of isotopic frequencies ν^i/ν for [^{18}O]-**2** and **2**. — [d] Calculated frequencies have been scaled with 0.9. — [e] Approximate description. — [f] Due to the splitting into several components the assignment of vib. 28 and vib. 27 is only tentative. The pattern of absorptions observed in the carbonyl region strongly depends on isotopic substitution.

the observed shifts are less than 20 cm^{-1}. The experimental values for acetone and for *p*-benzoquinone are 30 and 31 cm^{-1}, respectively, corresponding to approximately 80% C=O stretching[20].

The carbonyl absorptions of **1** are generally at lower frequencies than those of the corresponding quinones (Table 3), which indicates a weaker C=O bond in **1**. The differences range from 27 in **12** to 122 cm^{-1} in **6**. These differences Δ are mostly of electronic origin, because substituents at C(2) and C(6) should not interact sterically with a carbonyl or diazo group at C(4), and even substituents at C(3) and C(5) should not experience much steric difference between C=O and C=N=N.

A comparison of **2**, **10**, and **12** reveals the influence of benzoannellation on $\nu_{C=O}$ and $\nu_{N\equiv N}$. While $\nu_{C=O}$ increases on double benzoannellation by 32.8 cm^{-1}, $\nu_{N\equiv N}$ decreases by 16.4 cm^{-1}. This indicates a smaller coupling between the diazo and carbonyl groups in **12** compared to **2** (Table 3). In **12** the value of $\nu_{C=O}$ is close to the 1674 cm^{-1} reported for the carbonyl absorption in matrix-isolated benzophenone[21], while in **10** it is halfway between **2** and **12**. The influence of benzoannellation on $\nu_{N\equiv N}$ is less pronounced, and one benzo group in **10** has a markedly smaller effect than two benzo groups in **12**, in good agreement with the NMR results.

Alkyl substituents at C(2) and C(6), as in **3** and **5**, cause small red shifts of both the $\nu_{C=O}$ and $\nu_{N\equiv N}$ vibrations, whereas methyl groups at C(3) and C(5) cause a small blue shift of $\nu_{C=O}$ and red shift of $\nu_{N\equiv N}$. Again, as was observed in the NMR spectrum, the influence of alkyl groups is small. The red shift of $\nu_{N\equiv N}$ is explained by the destabilization of resonance structures **1B** and **1C** by electron-donating alkyl groups, thus increasing the weight of **1A**.

The largest shifts for both $\nu_{C=O}$ and $\nu_{N\equiv N}$, and the largest differences Δ from the corresponding quinone $\nu_{C=O}$ absorptions, are observed with electron-accepting groups at C(2) and C(6) as in **6**–**9**. Large red shifts of $\nu_{C=O}$ are accompanied by blue shifts of $\nu_{N\equiv N}$. The blue shift of $\nu_{N\equiv N}$ is readily explained by the increasing contribution of resonance structure **1C**, while $\nu_{C=O}$ also reflects special interactions of the

Table 7. IR-spectroscopic data of quinone diazides **2**–**12**, matrix-isolated in argon at 10 K. Wavenmumbers in cm^{-1}, relative intensities, approximate description

2: ν = 2085.1 (s), 2078.2 (s), 2075.8 (vs, $\nu_{N\equiv N}$), 1635.6 (vs, $\nu_{C=O}$), 1628.2 (s), 1626.4 (s), 1617.1 (s), 1455.4 (w), 1406.4 (w), 1269.4 (vw), 1251.1 (w), 1241.4 (s), 1145.3 (s), 1095.4 (vw), 845.6 (m), 790.7 (w), 772.4 (w), 717.7 (m) cm^{-1}.

[D$_4$]-**2**: ν = 2078.6 (vs, $\nu_{N\equiv N}$), 1630.1 (s, $\nu_{C=O}$), 1617.0 (s), 1597.6 (s), 1562.0 (s), 1416.0 (w), 1304.2 (m), 1236.4 (w), 1140.1 (w), 1009.6 (vw), 830.2 (m), 813.8 (w), 745.4 (m), 736.2 (w), 664.9 (vw), 657.5 (m) cm^{-1}.

2-O^{18}: ν = 2084.6 (s), 2078.1 (s), 2075.1 (vs, $\nu_{N\equiv N}$), 1635.6 (m, $\nu_{C=O}$), 1618.9 (m), 1612.5 (s), 1564.0 (w), 1454.5 (w), 1403.2 (w), 1267.0 (vw), 1252.1 (w), 1241.4 (s), 1144.8 (m), 1094.9 (vw), 842.9 (w) 788.3 (vw), 770.4 (vw), 712.7 (vw) cm^{-1}.

3: ν = 2931.3 (4, $\nu_{C\text{-}H}$), 2089.5 (6), 2068.8 (100, $\nu_{N\equiv N}$), 2064.4 (100), 2053.3 (11), 1618.0 (49, $\nu_{C=O}$), 1608.3 (44, $\nu_{C=O}$), 1592.9 (9), 1455.5 (3), 1428.5 (4), 1382.7 (7), 1379.3 (5), 1365.8 (4), 1254.9 (34), 1135.4 (7), 1011.0 (9), 932.4 (4), 872.1 (9), 531.3 (6) cm^{-1}.

4: ν = 2090.5 (6), 2070.7 (100, $\nu_{N\equiv N}$), 2067.3 (33), 2062.0 (12), 2059.1 (14), 2052.4 (14), 1634.4 (100, $\nu_{C=O}$), 1618.5 (9), 1607.9 (2), 1599.7 (2), 1596.3 (3), 1464.2 (4), 1434.8 (4), 1359.6 (2), 1354.3 (8), 1350.4 (15), 1284.4 (2), 1280.5 (4), 1239.0 (11), 907.3 (2), 904.0 (3), 875.0 (4), 708.2 (4) cm^{-1}.

5: ν = 3018.5 (1, $\nu_{C\text{-}H}$), 2963.6 (6, $\nu_{C\text{-}H}$), 2943.3 (2, $\nu_{C\text{-}H}$), 2926.0 (2, $\nu_{C\text{-}H}$), 2892.7 (2, $\nu_{C\text{-}H}$), 2875.3 (1, $\nu_{C\text{-}H}$), 2066.4 (100, $\nu_{N\equiv N}$), 1636.8 (3), 1630.5 (2), 1607.9 (11), 1596.3 (33, $\nu_{C=O}$), 1582.3 (4), 1489.7 (6), 1457.4 (4), 1423.2 (1), 1388.0 (7), 1354.7 (12), 1278.6 (4), 1254.5 (6), 1196.1 (14), 935.8 (3), 922.8 (4), 888.1 (6), 886.1 (5) cm^{-1}.

6: ν = 2101.1 (69, $\nu_{N\equiv N}$), 2095.3 (32), 2086.6 (41), 2082.3 (51), 2076.5 (100, $\nu_{N\equiv N}$), 1660.9 (14), 1648.8 (60), 1645.0 (25), 1638.7 (26), 1632.9 (19), 1631.5 (19), 1579.9 (61), 1203.8 (66), 1189.9 (28), 1187.0 (18), 1181.2 (12), 896.7 (20), 807.1 (18), 805.6 (13), 798.9 (13) cm^{-1}.

7: ν = 2090.0 (88), 2088.0 (92), 2085.6 (100, $\nu_{N\equiv N}$), 2054.3 (10), 1659.9 (3), 1643.5 (21), 1635.3 (7), 1607.9 (5), 1575.6 (38), 1350.9 (2), 1195.2 (39), 1184.6 (4), 864.9 (9), 735.2 (17), 727.0 (3) cm^{-1}.

8: ν = 2113.6 (s, $\nu_{N\equiv N}$), 2092.9 (w), 2057.2 (vw), 1740.9 (w), 1595.8 (vs, $\nu_{C=O}$), 1564.0 (vw), 1535.1 (w), 1481.1 (m), 1473.3 (s), 1458.4 (w), 1379.3 (w), 1335.0 (vw), 1260.3 (vw), 1204.3 (vw), 1164.8 (s), 1127.2 (w), 838.9 (vw), 528.9 (vw) cm^{-1}.

9: ν = 2281.9 (vw), 2212.4 (w), 2175.3 (w), 2129.0 (s), 2121.3 (s), 2116.5 (s), 2104.4 (vs, $\nu_{N\equiv N}$), 2098.2 (vs), 2080.8 (vw), 2073.1 (w), 1773.7 (w), 1742.4 (s, $\nu_{C=O}$ Carboxyl), 1728.9 (s, $\nu_{C=O}$ Carboxyl), 1617.5 (m), 1605.4 (vs, $\nu_{C=O}$), 1599.2 (vs, $\nu_{C=O}$), 1565.0 (vs), 1536.5 (m), 1492.2 (vs), 1478.2 (s), 1459.4 (s), 1433.3 (m), 1382.2 (w), 1358.6 (s), 1240.5 (m), 1227.5 (vs), 1182.6 (m), 1176.8 (s), 1106.9 (s), 1039.0 (vw), 1010.0 (w), 952.7 (w), 926.1 (w), 923.3 (w), 907.5 (w), 898.7 (w), 807.1 (w), 688.9 (vw), 667.2 (vw), 648.9 (vw), 535.6 (m) cm^{-1}.

10: ν = 2071.7 (100, $\nu_{N\equiv N}$), 2051.4 (5), 1645.9 (27), 1643.5 (36, $\nu_{C=O}$), 1636.8 (11), 1624.3 (4), 1610.3 (9), 1600.7 (10), 1585.7 (8), 1556.8 (4), 1482.5 (10), 1471.4 (2), 1293.5 (3), 1272.3 (12), 1224.6 (8), 1152.7 (5), 1148.9 (4), 1133.0 (2), 1014.9 (2), 826.3 (2), 756.0 (5), 688.5 (2) cm^{-1}).

11: ν = 2085.2 (3), 2062.0 (100, $\nu_{N\equiv N}$), 2052.4 (12), 1635.8 (33, $\nu_{C=O}$), 1627.6 (7), 1605.9 (32), 1600.6 (9), 1484.0 (13), 1304.1 (24), 1211.1 (18), 1073.7 (5), 1033.7 (9), 1014.5 (4), 941.6 (5), 756.4 (10), 694.7 (5) cm^{-1}.

12: ν = 3071.6 (1, $\nu_{C\text{-}H}$), 3035.9 (1, $\nu_{C\text{-}H}$), 2077.0 (9), 2059.6 (100, $\nu_{N\equiv N}$), 2057.7 (99), 2052.9 (36), 1657.5 (50, $\nu_{C=O}$), 1649.8 (11), 1646.9 (12), 1645.0 (12), 1610.8 (21), 1604.5 (14), 1602.6 (16), 1578.9 (6), 1491.7 (18), 1485.9 (14), 1482.0 (14), 1310.4 (8), 1307.0 (7), 1302.2 (23), 1296.4 (16), 1274.2 (11), 1271.3 (9), 1171.1 (13), 1168.7 (15), 1134.4 (5), 931.9 (15), 758.9 (10), 626.8 (5) cm^{-1}.

carbonyl group with the neighbouring substituents, especially hydrogen bonds in **8** and **9**. The very high value of $\nu_{N\equiv N}$ (2114 cm^{-1}) for **8** again demonstrates a large extent of charge transfer from the diazo to the carbonyl group.

Conclusion

p-Benzoquinone diazides **1** are molecules with unusual structural and bond properties. A comparison of their structural and spectroscopic data with those of reference compounds such as diazofluorene **13** or *p*-benzoquinone reveals the strong interaction between the carbonyl and diazo group. Notable are the lengthening of the C(1)–O and C(4)–N(1) bonds, the upfield shift of the ^{13}C-NMR resonance of C(1) and downfield shift of C(4), and the low IR frequency of the C=O str. mode. All these observations indicate a significant contribution of the "aromatic" resonance structure **1D** to the electronic structure of **1**, although **1A** and **1B** are still of major importance.

The interaction between the carbonyl and diazo group is not much influenced by alkyl substituents either at C(2) and C(6) or C(3) and C(5), but decreases on benzoannellation. Thus, **12** displays properties similar to "ordinary" aromatic ketones or diazo compounds. The largest influence is observed with electron-withdrawing substituents and especially with carboxy groups at C(2). Compounds **8** and **9** are characterized by very strong intramolecular hydrogen bonds and spectroscopic and bond properties halfway between diazo and diazonium compound, indicating considerable charge transfer from the diazo to the diazonium group.

We thank the *Deutsche Forschungsgemeinschaft*, the *Bundesminister für Forschung und Technologie* (07EU761, EUROTRAC Subproject LACTOZ), and the *Fonds der Chemischen Industrie* for financial support.

Experimental

Calculations: The ab initio calculations were carried out using TURBOMOLE[22,23] and standard basis sets. MOPAC (version 6)[24] was used for the semiempirical AM1[12] calculations.

^{1}H- and ^{13}C NMR: 400.1 and 100.6 MHz, respectively (Bruker AM 400), in CDCl$_3$ as solvent if not stated otherwise, (CH$_3$)$_4$Si internal standard. – MS (EI, 70 eV): Varian MAT CH7 or MAT 8222. – Elemental analyses: Institut für Pharmazeutische Chemie, Technische Universität Braunschweig. – All reactions were carried out under nitrogen. The synthesis of **2**, [D$_4$]-**2**, [^{18}O]-**2** has been described in ref.[25], the syntheses of **3**, **4**, **6**, **7**, **10**, and **11** in ref.[3] Single crystals of **2** for the determination of the X-ray structure were obtained by slow diffusion of dry ether into a saturated solution of **2** in dry ethanol at –20 °C (orange-yellow needles). Under these conditions the crystals did not contain water.

3-Diazo-6-oxo-1,4-cyclohexadiene-1-carboxylic Acid (**8**) was synthesized by diazotization of 5-aminosalicylic acid (Aldrich) according to the procedure of Ried and Appel[26]. The product was recrystallized from acetone/water (1:1) (57%). Single crystals for the determination of the X-ray structure were obtained by slow crystallisation from CH$_3$CN/H$_2$O (1:1). Brown needles, m.p. 164 °C (dec.) (ref.[27] 162 °C). Conditions of matrix isolation: 130 °C, electrically heated oven. – ^{1}H NMR ([D$_6$]DMSO): $\delta = 16.04$ (s, br), 8.90 (d, $J_m = 2.7$ Hz), 8.11 (dd, $J_{cis} = 9.6$, $J_m = 2.8$ Hz), 6.73 (d, $J_{cis} = 9.5$ Hz). – ^{1}H NMR (CF$_3$CO$_2$D): $\delta = 8.72$ (d, $J_m = 2.6$ Hz), 8.04 (dd, $J_{cis} = 9.3$, $J_m = 2.6$ Hz), 6.96 (d, $J = 9.3$ Hz). – ^{13}C NMR ([D$_6$]DMSO): $\delta = 87.0$, 119.4, 123.9, 134.8, 138.9, 165.7, 180.2. – ^{13}C NMR (CF$_3$CO$_2$D): $\delta = 103.6$, 118.1, 125.7, 140.3, 141.5, 172.4, 175.4. – MS (FAB, NBA Matrix, pos.), *m/z* (%): 165 (18) [M$^+$ + 1], 138 (27), 137 (58), 136 (Carbene, 68). – C$_7$H$_4$N$_2$O$_3$ (164.1): calcd. C 51.21, H 2.46, N 17.07; found C 51.30, H 2.47, N 17.03.

3-Diazo-5-methyl-6-oxo-1,4-cyclohexadiene-1-carboxylic Acid (**9**) was synthesized by diazotization of 5-amino-3-methylsalicylic acid according to the procedure of Ried and Appel[26]. The product was recrystallized from acetone/water (1:1) (40%). Yellow needles, m.p. 155°C (dec.) (ref.[27] 156°C). – ^{1}H NMR ([D$_6$]DMSO): $\delta = 13.53$ (s, 1H), 8.85 (d, 1H, $J_m = 2.9$ Hz), 7.99 (m), 2.08 (d, 3H, $J = 0.7$ Hz). – ^{1}H NMR (CF$_3$CO$_2$D): $\delta = 9.14$ (d, 1H, $J_m = 2.6$ Hz), 8.39 (d, 1H, $J_m = 2.3$ Hz), 2.51 (s, 3H). – ^{13}C NMR ([D$_6$]DMSO): $\delta = 15.9$, 85.9, 118.2, 131.3, 133.0, 137.9, 166.1, 179.8. – ^{13}C NMR (CF$_3$CO$_2$D): $\delta = 17.0$, 102.5, 116.9, 138.0, 138.3, 139.4, 172.9, 174.4. – MS, *m/z* (%): 179 (4), 178 (31) [M$^+$], 150 (55), 135 (5), 134 (44), 123 (4), 122 (64), 107 (6), 106 (64), 105 (10), 93 (8), 79 (5), 78 (20), 77 (100), 74 (10), 67 (22), 66 (9), 54 (4), 52 (16), 51 (18), 50 (38), 49 (20), 43 (4).

10-Diazo-9(10H)-anthracenone (9-Diazo-10-anthrone) (**12**) was synthesized by diazo group transfer to anthrone (Jansen) according to the method by Regitz[28]. Single crystals for the determination of the X-ray structure were obtained by slow diffusion of pentane into a saturated solution of **12** in CHCl$_3$ at -20°C. Red-brown crystals, m.p. >250°C. Conditions of matrix isolation: 63°C, electrically heated oven. – ^{1}H NMR (CDCl$_3$): $\delta = 8.50$ (dd, $J_o = 8.0$, $J_m = 1.2$ Hz), 7.66 (m), 7.37 (m), 7.27 (d, $J_o = 7.5$ Hz). – ^{13}C NMR (CDCl$_3$): $\delta = 64.5$, 120.6, 125.2, 128.3, 128.9, 129.7, 132.9, 179.9. – MS, *m/z* (%): 221 (2), 220 (14) [M$^+$], 194 (9), 193 (12), 192 (60), 165 (23), 164 (100), 163 (82), 162 (13), 161 (5), 137 (8), 96 (8), 91 (14), 82 (16), 81 (16), 44 (29). – C$_{14}$H$_8$N$_2$O: calcd. 220.0636, found 220.0636 ± 2 ppm.

Matrix Spectroscopy: Matrix-isolation experiments were performed by standard techniques with an Air Products CSW-202 Displex closed-cycle helium cryostat. Argon (Linde, 99.9999%) was deposited at 28–30 K on top of a CsI (IR experiments) or sapphire (UV-Vis experiments) window with a rate of approximately 0.15 mmol/min. An electrically heated oven was used for the deposition of the quinone diazides. Infrared spectra were recorded using a Bruker IFS66 FTIR spectrometer, a standard resolution of 1 cm^{-1} in the range 4000–450 cm^{-1} was used. UV-Vis spectra were recorded on a Hewlett-Packard 8452A diode array spectrophotometer with 2-nm resolution.

X-Ray Structure Determinations: Data collection and reduction: Crystals were mounted on glass fibres in inert oil and transferred to the cold gas stream of the diffractometer (**2**, **5**, **8**: Stoe STADI-4; **12**, Siemens R3). **2**, **5**, **8**: Cell constants were refined from $\pm\omega$ angles of ca. 50 reflections in the 2Θ range 20–23°; **12**: The orientation matrix was refined from setting angles of 50 reflections in the same range. Monochromated Mo-K_α radiation ($\lambda = 71.073$ pm) was employed. – *Structure solution and refinement:* The structures were solved by direct methods and refined anisotropically on F^2 (program system: SHELXL-92, G. M. Sheldrick, unpublished). All H atoms were identified in difference Fourier syntheses and then included by using a riding model. Weighting schemes of the form $w^{-1} = [\sigma^2(F_o^2) + (aP)^2 + bP]$ were employed, with $P = (F_o^2 + 2F_c^2)/3$. Crystal data are compiled in Table 8[29]. – *Special features of refinement:* Compound **2** crystallizes with two independent molecules. The crystal quality of compound **5** was only moderate and the *R* values are correspondingly high; in order to stabilize the refinement, 165 restraints on displacement parameters were incorporated. Compounds **8** and **12** crystallize in non-centrosymemtric space groups; the absolute structures could not be determined because the anomalous scattering contribution is too small. The origins were fixed by using the method of Flack and Schwarzbach[30]. For **8**, 102 displacement parameter restraints were employed. Compound **12** crystallizes with four independent molecules; because of insufficient data, chemically equivalent bond lengths and angles were restrained to be approximately equal in addition to the restraints on displacement parameters (1237 restraints in all).

Table 8. Crystal data of quinone diazides **2**, **5**, **8**, and **12**

Compound	**2**	**5**	**8**	**12**
Formula	$C_6H_4N_2O$	$C_{14}H_{20}N_2O$	$C_7H_4N_2O_3$	$C_{14}H_8N_2O$
M_r	120.11	232.32	164.12	220.22
Crystal habit	Orange prism	Orange tablet	Yellow prism	Orange tablet
Crystal size (mm)	0.75 x 0.4 x 0.35	0.3 x 0.3 x 0.2	0.8 x 0.5 x 0.2	0.75 x 0.65 x 0.2
Space group	$P2_1/c$	$P2_1/c$	Cc	$Pca2_1$
Temperature (°C)	-130	-130	-130	-95
Cell constants :				
a (pm)	1265.0(4)	941.5(4)	373.12(6)	737.5(2)
b (pm)	776.7(3)	1183.6(6)	1547.8(2)	2719.5(5)
c (pm)	1212.9(4)	1230.2(5)	1124.6(3)	2036.5(4)
β (°)	109.66(3)	91.11(3)	94.48(2)	
V (nm^3)	1.1222(7)	1.3706(11)	0.6475(2)	4.085(2)
Z	8	4	4	16
D_x (Mg m^{-3})	1.422	1.126	1.684	1.433
$F(000)$	496	504	336	1824
μ (mm^{-1})	0.10	0.07	0.14	0.09
$2\theta_{max}$ (°)	55	50	55	50
No. of reflections :				
measured	3555	3607	1079	3727
independent	2595	2422	980	3723
R_{int}	0.016	0.124	0.024	0.016
$wR(F^2$, all refl.)	0.111	0.213	0.087	0.140
$R(F, >4\sigma(F))$	0.043	0.094	0.032	0.044
No. of parameters	163	160	110	613
No. of restraints	0	165	102	1237
S	1.1	1.1	1.1	1.1
Max. Δ/σ	<0.001	<0.001	<0.001	<0.001
Max. $\Delta\rho$ (e pm^{-3} x10^6)	0.16	0.19	0.24	0.21

---

[1] V. V. Ershov, G. A. Nikiforov, C. R. I. de Jonge, *Quinone Diazides*, Elsevier, Amsterdam 1981.
[2] S. P. Walch, W. A. Goddard III, *J. Am. Chem. Soc.* **1975**, *97*, 5319–5330.
[3] G. Bucher, W. Sander, *J. Org. Chem.* **1992**, *57*, 1346–1351.
[4] G. Bucher, W. Sander, *Chem. Ber.* **1992**, *125*, 1851–1859.
[5] T. H. Tulip, P. W. R. Corfield, J. A. Ibers, *Acta Crystallogr., Sect. B*, **1978**, *34*, 1549–1555.
[6] C. Römming, *Acta Chem. Scand.* **1963**, *17*, 1444–1454.
[7] C. T. Presley, R. L. Sass, *Acta Crystallogr., Sect. B*, **1970**, *26*, 1195–1198.
[8] H. R. Luss, D. L. Smith, *Acta Crystallogr., Sect. B*, **1972**, *28*, 884–889.
[9] P. B. Rees, *Acta Crystallogr., Sect. B*, **1970**, *26*, 1298–1303.
[10] S. L. Baughcum, R. W. Duerst, W. F. Rowe, Z. Smith, E. B. Wilson, *J. Am. Chem. Soc.* **1981**, *103*, 6296–6303.
[11] M. Ichikawa, *Acta Crystallogr., Sect. B*, **1978**, *34*, 2074–2080.
[12] M. J. S. Dewar, E. G. Zoebisch, E. F. Healy, J. J. P. Stewart, *J. Am. Chem. Soc.* **1985**, *107*, 3902–3909.
[13] S. D. Kahn, W. J. Hehre, J. A. Pople, *J. Am. Chem. Soc.* **1987**, *109*, 1871–1873.
[14] R. O. Duthaler, H. G. Förster, J. D. Roberts, *J. Am. Chem. Soc.* **1978**, *100*, 4974–4979.
[15] C. Casewit, J. D. Roberts, *J. Org. Chem.* **1982**, *47*, 2875–2878.
[16] S. Berger, A. Rieker, *Tetrahedron* **1972**, *28*, 3123–3399.
[17] G. A. Bell, I. R. Dunkin, *J. Chem. Soc., Faraday Trans. 2*, **1985**, *81*, 725–734.

[18] K. B. Whetsel, G. F. Hawkins, F. E. Johnson, *J. Am. Chem. Soc.* **1956**, *78*, 3360–3363.

[19] [19a] E. D. Becker, E. Charney, T. Anno, *J. Chem. Phys.* **1965**, *42*, 942–949. – [19b] E. Charney, E. D. Becker, *J. Chem. Phys.* **1965**, *42*, 910–913.

[20] S. Pinchas, I. Laulicht, *Infrared Spectra of Labelled Compounds*, Academic Press, London, **1971**.

[21] W. Sander, *J. Org. Chem.* **1989**, *54*, 333–339.

[22] M. Häser, R. Ahlrichs, *J. Comput. Chem.* **1989**, *10*, 104–111.

[23] R. Ahlrichs, M. Bär, M. Häser, H. Horn, C. Kölmel, *Chem. Phys. Lett.* **1989**, *93*, 165.

[24] M. J. S. Dewar, *QCPE*, **1990**, *506*.

[25] W. Sander, G. Bucher, F. Reichel, D. Cremer, *J. Am. Chem. Soc.* **1991**, *113*, 5311–5322.

[26] W. Ried, H. Appel, *Liebigs Ann. Chem.* **1961**, *646*, 82–95.

[27] A. Rugeddi, *Gazz. Chim. Ital.* **1929**, 13.

[28] R. Regitz, *Chem. Ber.* **1964**, *97*, 2742–2754.

[29] Further details of the structure determinations have been deposited at the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen, Federal Republic of Germany. Any request for this material should quote the full literature citation and the reference numbers CSD-400134, 400135, 400136, and 400137.

[30] H. D. Flack, D. Schwarzenbach, *Acta Crystallogr., Sect. A*, **1988**, *44*, 499.

[98/93]