Diazo Compounds

PROPERTIES and SYNTHESIS

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Gerhard Mass

Diazo Compounds

Properties and Synthesis

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Dedicated to Bernd Eistert

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Preface

The discovery of the chemistry of aliphatic diazo compounds was made a century ago: Theodor Curtius synthesized ethyl diazoacetate in 1883 for the first time and with this opened the wide field of diazo chemistry, which even today has not yet been exhausted. The solution of the long controversial problem of constitution, the development of general and facile syntheses, and the application of diazo compounds in organic synthesis, facilitated by their incredible reactivity, have made this field a truly exciting one. Novel methods of synthesis, such as diazo group transfer and electrophilic diazoalkane substitution, and the most valuable contribution of diazo compounds to the chemistry of carbenes and cycloadditions indicate the continued interest in these compounds.

This monograph deals only with the properties and syntheses of aliphatic diazo compounds. Discussions concerning their reactions — if not absolutely necessary to describe certain aspects of their preparation — have been intentionally omitted in order to maintain the format. The first chapters deal with structure, spectroscopic properties, thermal behavior, acidic decomposition, and photochemistry of diazoalkanes, followed by synthetic methods. Further initiatives and developments may be expected, especially from the discoveries of novel diazoalkane syntheses. The Bibliography is intended to make entry into the tremendously growing literature on the subject easier.

This monograph was primarily written to be used by chemists interested in the synthetic application of diazo compounds and for colleagues with an interest in the physical properties of these compounds. We hope to stimulate

those who, like the authors, believe that the chemistry of diazoalkanes will continue to be nourished by the imagination of its disciples.

Throughout the various chapters of the book, the literature up to the end of 1982 has been reviewed. The major developments published up to January of 1986 are compiled concisely in an Addendum.

We are grateful to Professor Peter Stang, University of Utah, on whose suggestion this monograph was written. Our thanks are also extended to the editors and staff of Academic Press for their patience and helpfulness.

We appreciate very deeply the skillful preparation of the artwork by our co-workers B. Feith, O. Göttel, A. Kuhn, W. Lorenz, W. Rösch, B. Singer, and U. J. Vogelbacher. Furthermore, our thanks go to Mrs. H. Mai for the careful typing of the manuscript.

Part I

Properties of Aliphatic Diazo Compounds

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Chapter 1

Structure and Spectroscopic Properties

1.1 The Constitution of Diazoalkanes

When Curtius first synthesized ethyl diazoacetate via amine diazotation in 1883, no suggestion was made as to whether the CN_2 group was in a cyclic [e.g., diazirine **1** (R = H)] or an open (**2**, R = H) configuration (*1*). Some years later, however, he postulated structure **1** for α-diazoesters, α-diazo-amides, and the salts of the free acids (*1a*). The cyclic structure was adopted for diazomethane by v. Pechmann, who had synthesized the compound by base cleavage of *N*-methyl-*N*-nitrosourethane in 1894 (*2*).
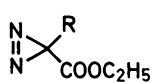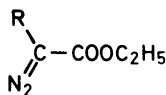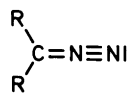
| 1 | 2 | 3 |

Thiele finally suggested open configuration **3** for diazoalkanes in 1911 (*3*); it contains, according to the valence theory accepted then, a pentavalent nitrogen atom. His reasoning is based on the experimental results that diazo compounds are formed by dehydrogenation of hydrazones, compounds whose open constitution was well known.

Neither chemical properties of diazo compounds nor measurements of the parachor or dipole moment of diazomethane could end the long-lived discussion over the "true" structure. An electron diffraction experiment by Boersch in 1935 finally decided the issue in favor of an open diazomethane

molecular structure with linear geometry of the CN_2 group (*4*). Only in 1957, did a chemical experiment prove the open structure for ethyl diazoacetate as well (*5*). Ethyl glycinate was diazotized with ^{15}N-labeled sodium nitrite, and the labeled ethyl diazoacetate reductively cleaved to glycine and ammonia. It was to be expected that in the case of a linear arrangement of the diazo group, ^{15}N would be released exclusively as ammonia, whereas for a cyclic arrangement a statistical distribution of the label between both reduction products should result. Analyses unambiguously decided in favor of the open structure.

Since 1960, straightforward routes to synthesize the cyclic valence isomer of diazomethane, diazirine **4** ($R^1 = R^2 = H$), and derivatives, have been discovered (*6,7*). This has made it possible to compare both classes of compounds directly: diazirines are (almost) colorless and most diazoalkanes are intensely yellow to red; diazirines are far less reactive than diazoalkanes (e.g. they are stable against acids), whereas sensitivity to acids is one of the most pronounced properties of most diazoalkanes (see Chapter 3, Section 1).
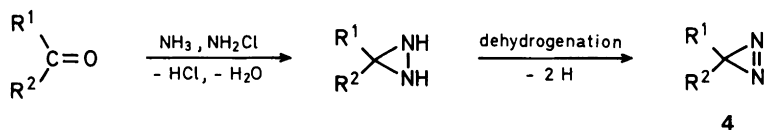
When suitable substituents are present, the valence isomerization diazoalkane–diazirine is possible in both directions. Upon irradiation of diazirine (*8*) ($\lambda = 320$ nm), 3-aryl-3*H*-azirines (*8a*) ($\lambda \geq 280$ nm), cycloalkanespirodiazirines (*8b*) ($\lambda \geq 310$ nm) or 3-*n*-butyl-3-phenyldiazirine (*8c*) ($\lambda \geq 330$ nm), isomerization to the corresponding diazoalkane competes with fragmentation into carbene and N_2. In these cases, diazoalkane formation was proved by trapping reactions, spectroscopically, or by the isolation of products that stem from diazoalkane reactions. In other examples, the intermediacy of diazoalkanes in thermal or photochemical reactions of diazirines was deduced from kinetic evidence or isotope labeling experiments (*8d*). 3,3-Diphenyldiazirine probably rearranges to diazodiphenylmethane in the presence of oxygen or mercury(II) oxide during its attempted synthesis (*9*). On the other hand, α-diazoamides (*5*) with a hydrogen atom at the diazo carbon will isomerize to the corresponding diazirinecarboxamides when irradiated with visible light (*10,11*).
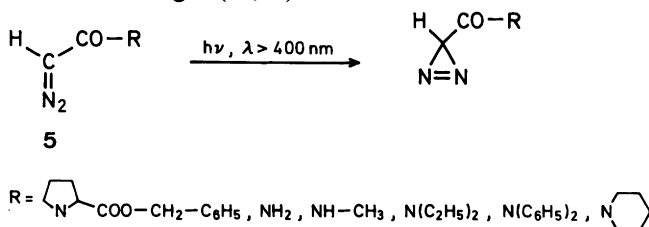
A reversible photochemical rearrangement of diazirine **6** and diazoalkane **7** is possible by selecting the appropriate wavelength. At 310 nm, **6** is converted to **7**; at 410 nm, the reverse reaction takes place. To some extent, carbenes are formed by N_2 elimination from the two valence isomers and undergo subsequent reactions (*12*).
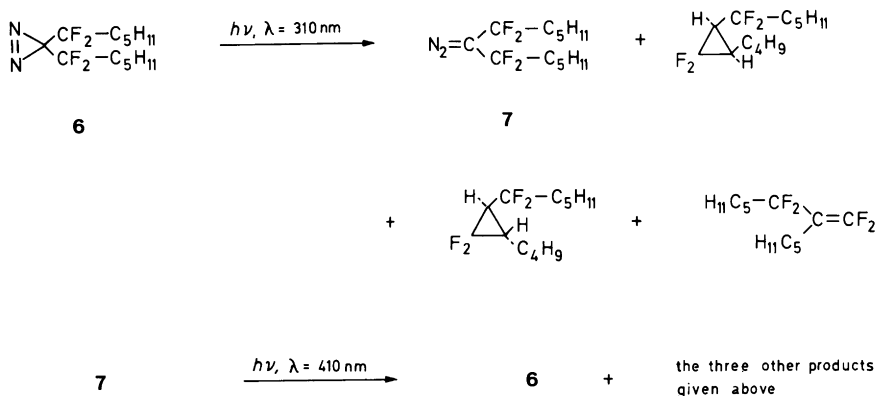
Examples of the thermal reversion of a photoisomerization are also known. Ultraviolet irradiation of 3-diazo-2,3-dihydro-2-indolone (3-diazo-2-oxoindoline) and its *N*-methyl derivative **8** leads to the pale yellow diazirines **9**, which rearrange, even at room temperature, to the red diazo compounds **8** (*13*). The activation parameters of **9** → **8** (R = CH_3) were determined as: $\Delta H^{\ddagger} = 110.9 \, \text{kJ mol}^{-1}$ (26.5 kcal mol^{-1}), $\Delta S^{\ddagger} = 40.6 \, \text{J K}^{-1} \, \text{mol}^{-1}$ (9.7 cal K^{-1} mol^{-1}).
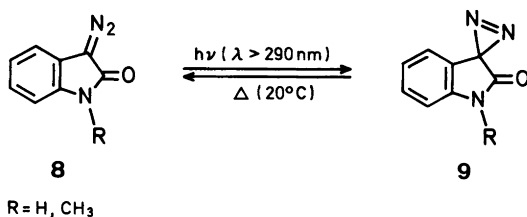
Isopropylidene diazomalonate **10** and the isomeric diazirine **11** show similar behavior (*14*).

$$H_2C = \overset{\oplus}{N} = \overset{\ominus}{\underline{N}}I$$

$$H_2\overset{\ominus}{C} - \overset{\oplus}{N} \equiv NI$$

$$\left[H - \overset{\ominus}{\underline{C}} = \overset{\oplus}{N} = \overset{\ominus}{\underline{N}}I \right.$$

$$\left. I\overset{\ominus}{C} \equiv \overset{\oplus}{N} - \overset{\ominus}{\underline{N}}H \right]$$

$$Li^{\oplus}$$

$$I\overset{\ominus}{C} \equiv \overset{\oplus}{N} - NH_2$$

$$IC = \bar{N} - NH_2$$

12

CH_3Li, $- CH_4$, H_2O, pH > 8,0

H_2O, pH < 6.0

CH_3Li, $- CH_4$
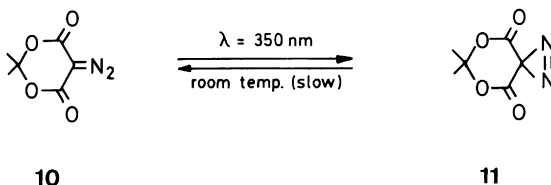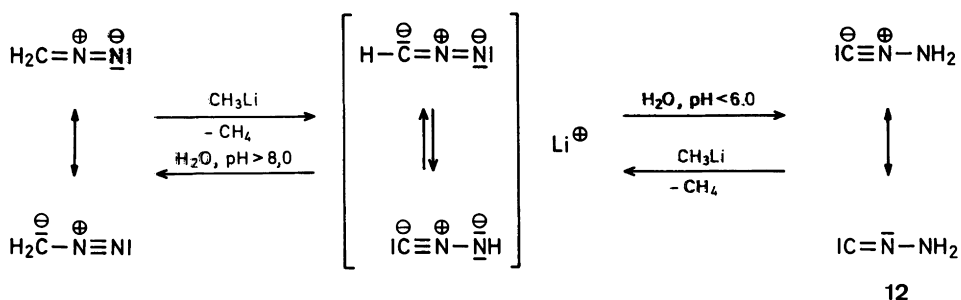
Scheme 1.1

It is not surprising that the thermal valence isomerization diazoalkane → diazirine has not yet been observed. Diazirine is higher in energy than diazomethane by a margin of ~ 126 kJ mol^{-1} (30 kcal mol^{-1}), according to the heats of formation obtained by mass spectrometric analysis (15,15a).

At a time when the structure of diazomethane was still in doubt, Müller and Kreutzmann (16) discovered another isomer. By treating the sodium salt of diazomethane in ether with acetic acid, a pale yellow solution is formed that no longer contains diazomethane but a new substance with unpleasant odor. The authors called the compound "isodiazomethane" but gave no suggested structure. Further investigations indicated the compound to be a tautomer of diazomethane, and it was finally characterized as N-isocyanoamine (**12**) because of the equivalency of both protons in the ^{1}H-NMR spectrum (17–19).

Scheme 1.1 demonstrates the reversible tautomerization of diazomethane and N-isocyanoamine, which takes place via a common tautomerizable anion.

For a long time there was a similar ambiguity in the constitution of α-diazocarbonyl compounds. Wolff (20) synthesized the compounds for the first time by diazotization of the α-amino derivatives of β-keto esters, or 1,3-diketones with sodium nitrite in dilute sulfuric acid solution. Because of their remarkable acid stability (see Chapter 3, Section 1), the open structure **13** seemed unlikely. Instead, Wolff suggested the structures of "diazoan-hydrides," such as compounds of the type **14** (1,2,3-oxadiazoles). However, such heterocycles have not been isolated yet.

13

14
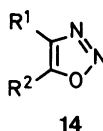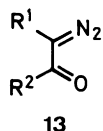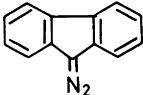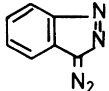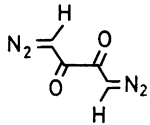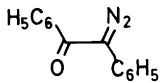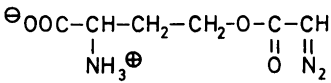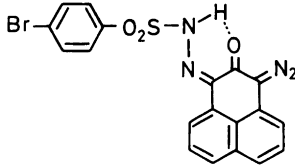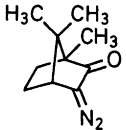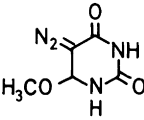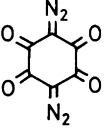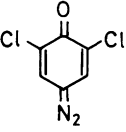
TABLE 1.1 Bond Geometry of the Diazo Group in Diazoalkanes[a]

Class of compounds	Compound		C—N (pm)	N—N (pm)	∡ CNN (deg)	∡ RCR' (deg)	Others	Ref.
Diazoalkanes	9-Diazofluorene		132.6 (4)	112.4 (4)	179.6 (3)	110.3 (3)		42
			132.1 (4)	112.7 (4)	179.5 (3)	110.1 (3)		
	3-Diazoindazole		133.8 (3)	111.0 (3)	179.6 (2)	111.9 (2)		43
α-Diazocarbonyl compounds	1,4-Bis(diazo)2,3-butanedione		131.3[c] (2)	111.4 (2)	176.8 (1)	116.3 (11)	C=O: 122.2 (2) C_N—C_O: 141.8 (2)	44
	2-Diazo-1,2-diphenyl-1-ethanone (azibenzil)		134.3	112.4			C=O: 120.8 C_N—C_O: 147.3	44a
	O-Diazoacetyl-L-serine		132.1 (9)[b,d]	113.7 (9)	179.3 (6)		C=O: 119.7 (6) 120.6 (7) C_N—C_O: 143.2 (7) 142.9 (8)	45

(continues)

TABLE 1.1 Bond Geometry of the Diazo Group in Diazoalkanes[a] (*Continued*)

Class of compounds	Compound	C—N (pm)	N—N (pm)	∢ CNN (deg)	∢ RCR' (deg)	Others	Ref.
	3-Diazo-2,3-dihydro-phenalene-1,2-dione-1-(4-bromo-phenylsulfonyl)-hydrazone	134.5 (12)	111.3 (12)	178.3 (11)	128.7 (9)	C=O: 123.0 (11) C_N—C_O: 142.5 (16)	46
	3-Diazo-1,7,7-tri-methyl-bicyclo-[2.2.1]heptan-2-one (3-Diazocamphor)	129.6 (8)	112.5 (8)	177.8 (8)		C=O: 121.5 (8) C_N—C_O: 144.8 (9)	47
	5-Diazo-6-methoxy-5,6-dihydrouracil	133.2[e]	111.3	[f]		C=O: 121.8 C_N—C_O: 143.6	48
	3,6-Bis(diazo)-1,2,4,5-cyclohexane-tetraone	135.7 (10)[c]	110.7 (10)	177.9 (9)	129.1 (7)	C=O: 120.8 (10) 121.4 (10) C_N—C_O: 143.7 (10) 143.3 (10)	22
p-Quinone-diazide	2,6-Dichloro-1,4-benzoquinone-4-diazide	137.4 (16)	109.6 (15)	178.9 (12)	124.2 (12)	C=O: 123.1 (16)	49

Heterosubstituted diazoalkanes	Diazophenyl(tri-phenylsilyl)-methane	$(C_6H_5)_3Si-\overset{\underset{\|}{N_2}}{C}-C_6H_5$	128.0 (17)	113.0 (16)	178.1 (14)	125.7 (8)	C—Si: 188.2 (17)	50
	Ethyl (tert-butylmer-curio)diazoacetate	$(CH_3)_3C-Hg-\overset{\underset{\|}{N_2}}{C}-\overset{\underset{\|}{O}}{C}-Et$	125 (4)	115 (5)	178 (5)	127 (2)	C—Hg: 212 (2) C=O: 121 (3) C_N-C_O: 138 (4)	51
	Mercury-bis(ethyl diazoacetate)	$EtO-\overset{\underset{\|}{O}}{C}-\overset{\underset{\|}{N_2}}{C}-Hg-\overset{\underset{\|}{N_2}}{C}-\overset{\underset{\|}{O}}{C}-OEt$	131 (2)[g]	108 (2)	175 (2)	126 (1)	C—Hg: 201 (1) C=O: 123 (2) C_N-C_O: 145 (2)	52
	Ethyl diazo(trimethyl-plumbyl)acetate	$(CH_3)_3Pb-\overset{\underset{\|}{N_2}}{C}-\overset{\underset{\|}{O}}{C}-OEt$	133[h,i]	117	174 (3)	130 (2)	C—Pb: 227 C=O: 125 C_N-C_O: 144	53
	Ethyl [Chloro-bis(tri-phenylphosphine)-palladium]diazo-acetate)	$[(C_6H_5)_3P]_2Pd-\overset{\underset{\|}{Cl}}{C}-\overset{\underset{\|}{N_2}}{C}-\overset{\underset{\|}{O}}{C}-OEt$	127 (2)	117 (2)	177.0 (13)	124.3 (9)	C—Pd: 201.0 (11) C=O: 122 (2) C_N-C_O: 145 (2)	54

[a] Values have been derived from X-ray analyses. Figures in parentheses are standard deviations.

[b] Two independent atoms.

[c] The molecule has a center of symmetry in the crystal.

[d] Measured at 0°C.

[e] Standard deviations ≤ 0.7 pm.

[f] No bond angles given.

[g] The molecule has C_2 symmetry.

[h] Measured at −50°C.

[i] Standard deviations 2–4 pm.

The product of diazotizing 1,4-diamino-2,3,5,6-tetrahydroxybenzene (*21*), which was long believed to have a bis-oxadiazole structure, was finally identified as 1,4-bis(diazo)cyclohexanetetraone **15** by X-ray analysis (*22*) (Table 1.1). This had been previously concluded from the NN and CO stretching frequencies in the infrared (IR) spectrum (*23*).

15
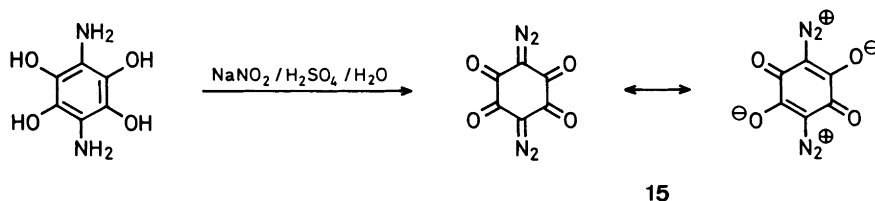
The X-ray analyses could also show that two originally claimed 1,2,3-oxadiazole-3-oxide structures, the products from *p*-hydroxycinnamic acid and nitrous acid (*24*) and from sorbic acid and N_2O_3 (*25*), are in reality 1,2,5-oxadiazole-2-oxides.

On the basis of photoelectron (PE) spectroscopy it has been postulated that 1,2-benzoquinone-1-diazide **16** is in equilibrium with its valence isomer 1,2,3-benzoxadiazole **17** in the gas phase. At 40°C there is an estimated 80–90% of oxadiazole, which would make it more stable, by $\sim 4 \, \mathrm{kJ \, mol^{-1}}$, than the diazocarbonyl form (*26*).

16   **17**
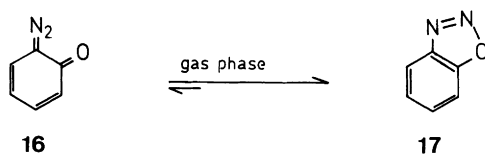
1.2 Structure and Bonding of Diazoalkanes

The linear structure of diazomethane (C_{2v} symmetry), derived from electron diffraction measurements (*4*) is confirmed by its microwave spectrum (*27*). A comparison of the experimental bond lengths with literature values (*28*) for the C—N and N—N bonds indicates the noninteger bond orders (Fig. 1.1.) A bond order of 2.66 for N—N and of 1.38 for N—C was derived from the force constants for the respective IR frequencies of $CH_2{}^{14}N^{15}N$ and $CH_2{}^{14}N_2$. The coupling force constants $f(\mathrm{NN/NC})$ indicate strong electronic coupling of the vibrations and extensive charge delocalization in the CN_2 group (*29*).

These results may be best explained with the resonance **18a** ↔ **18b** ↔ **18c** ↔ **18d**, where the resonance structures **18a** and **18b** are the main contributors. According to a valence bond calculation, a spin-paired

Compare: C—N   147 pm

C$\cdots$N   132 pm   (in OHC—NH$_2$)

N—N   144 pm

N=N   124 pm

N≡N   109,8 pm
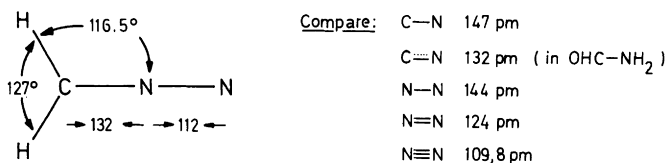
Fig. 1.1. Bond lengths (pm) and bong angles in diazomethane.

1,3-diradical **18e** with strong bonding interactions between its radical π orbitals might contribute significantly to the gound state of diazomethane (*30, 31*).
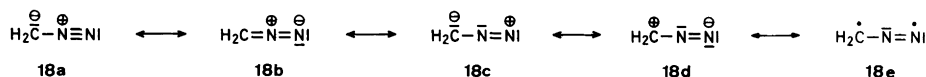
The linearity of the molecule makes sp^2 hybridization of the diazo carbon and sp hybridization of both nitrogen atoms plausible. Two of the six π electrons form the two-center π_y bond, and the other four, as pairs, occupy two three-center π_x molecular orbitals (*32*) [Fig. 1.2(a)].

According to the theory, the highest occupied molecular orbital (HOMO) in diazomethane is such a three-center orbital. It has a nodal plane perpendicular to the z axis containing the central N atom [Fig. 1.2(b)] and is therefore nonbonding (*33*). This corresponds in principle to the nonbonding three-center orbital of an allylic system. The shape and position of the first PE band of diazomethane (*34,35*) and 2-diazopropane (*36*) confirm this concept. The first ionization potential required to ionize this particular molecular orbital of diazomethane was determined as 9.03 eV by mass spectrometry, whereas the fragmentation that involves cleaving off nitrogen requires 12.3 eV (*15*).

$$H_2C{=}N_2 + e \longrightarrow CH_2N_2{}^+ + 2e \qquad 9.03 \pm 0.05\,eV$$

$$H_2C{=}N_2 + e \longrightarrow CH_2{}^+ + N_2 + 2e \qquad 12.3 \pm 0.1\ \,eV$$

(a)

(b)

Fig. 1.2. Bonding in diazomethane. (a) Atomic orbitals relevant for the π MOs. (b) $\Psi_{HOMO} = 2b_1(\pi)$; orbital coefficients as calculated by CNDO/2.

From the photoelectron spectra, the ionization potential for the HOMO of diazomethane was determined to be 9.00 eV (*34*); the value for 2-diazopropane is 7.88 eV (*36*). In diazocyclopentadiene, the $3b_1(\pi)$ and the $1a_2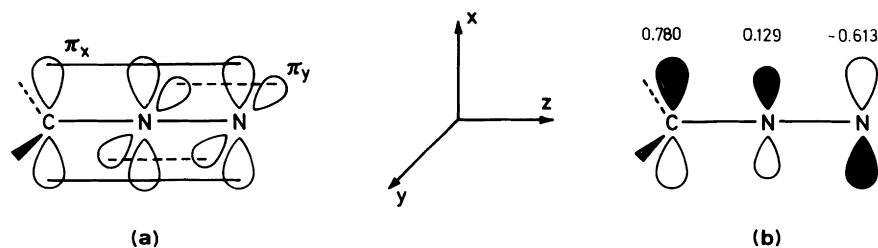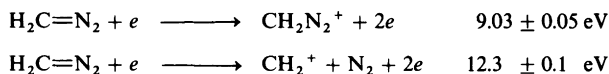(\pi)$ orbital are incidentally almost degenerate [ionization potentials: 8.37 ± 0.04 and 8.66 ± 0.03 eV (*36,37*)], which makes a correlation with the HOMO impossible. In this case, only $C(2p\pi)$ orbitals combine to the $1a_2(\pi)$ molecular orbital (MO), whereas the $3b_1(\pi)$ MO has additional $N(2p\pi)$ character with antibonding N—N and bonding N—C interactions.

The orbital energies of diazomethane have been calculated by using EH (*33*), *ab initio* (*38*), STO-3G (*34*), MINDO/2 (*39*), MINDO/3 (*34*), and CNDO/2 (*40*) methods. A graphic representation of the MOs as calculated *ab initio* appears in ref. *41*. The frontier orbitals of diazomethane are represented in a simplified form in Fig. 1.3, which also illustrates their pronounced similarity to those of ketenes and ketene imines.

Let us now consider the influence of substituents on the bond geometry of the diazo group (see Table 1.1) (*42–54*). In simple diazoalkanes like 9-diazofluorene (*42*), 2-bromo-9-diazofluorene (*55*), and 3-diazoindazole

$3b_1 \, (\pi^*_{CNN})$

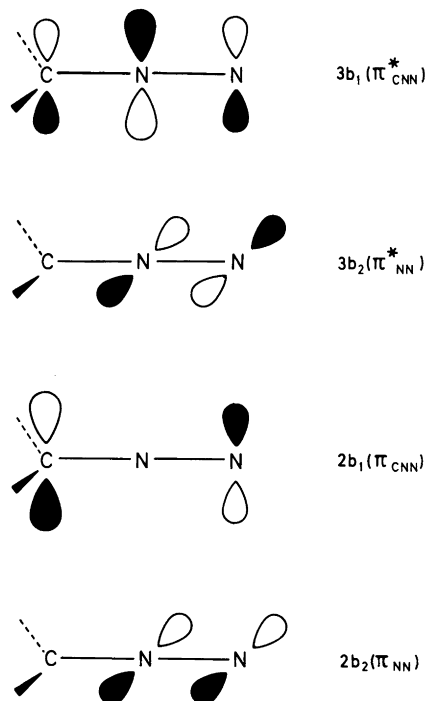$3b_2(\pi^*_{NN})$

$2b_1(\pi_{CNN})$

$2b_2(\pi_{NN})$

Fig. 1.3. Frontier orbitals in diazomethane.

(*43*), the geometry as described for diazomethane (Fig. 1.1) is maintained and with this the dominating participation of the resonance structures **18a** ↔ **18b** in bonding.

If the diazo group is located next to groups capable of conjugation, these as well are included more or less into the resonance, which results in the chemical properties of these compounds being significantly different from those of simple diazo compounds. The high dipole moment of diazomalono-nitrile (**19**) (*56*), for example, indicates considerable participation of the diazonium methanide resonance form in the ground state of the molecule.

19 ($\mu = 3.8$ D)   **20** ($\mu = 1.42$ D)   **21** ($\mu = 7.66$ D)   **22** ($\mu = 11.44$ D)
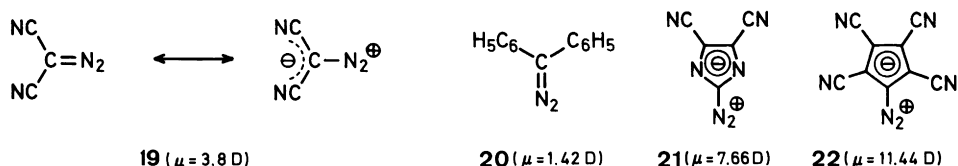
Even more pronounced is the difference between diazodiphenylmethane **20** (*57*), a "regular" diazoalkane, and 2-diazo-4,5-imidazole dicarbonitrile **21** (*58*) or even diazocyclopentadiene tetracarbonitrile **22** (*59*); the dipole moment of the latter resembles a diazonium compound rather than a diazo compound. The observed electrophilic reactions of the diazo group and the aromatic character of the five-membered ring allow the same conclusion; EH calculations further confirmed this (*32*).

The bond state for α-diazocarbonyl compounds may be described essen-tially by the resonance structures **23a–c**. It is important that the negative charge of the diazo carbon in **23a** can be shifted to the carbonyl group, whereby a diazoniumenolate structure **23c** is formed. For such structures, lengthening the C—N bond and shortening of the N—N bond (into the proximity of a N≡N bond distance) are expected.

23a   **23b**   **23c**
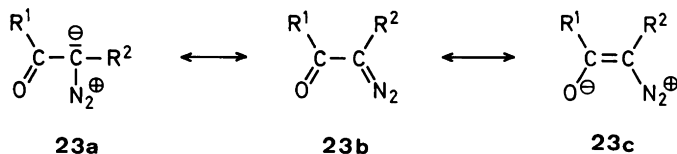
The few α-diazocarbonyl compounds that have been investigated so far seem to confirm a resonance for **23a–c**. Only in *O*-diazoacetyl-L-serine (*45*) is there a case of an α-diazocarbonyl group that is not disturbed by electronic, steric, and conjugative influences. The most significant indication of **23c** being the most important contributor to the bond state of a diazocarbonyl compound is found for 3-diazo-2,3-dihydrophenalene-1,2-dione-1-(4-bromo-phenylsulfonyl)hydrazone (*46*), where an intramolecular hydrogen bond further stabilizes this resonance structure.

In all examples in Table 1.1, the strict planarity of the (O)—C(O)—C(R)N$_2$ fragment is striking. This has to be interpreted as a consequence of the resonance **23a–c**.

On the other hand, the participation of aromatic resonance structures in the bond state of *o*- and *p*-quinonediazides (**24 and 25**) is not as pronounced as one might think.

24   **25**
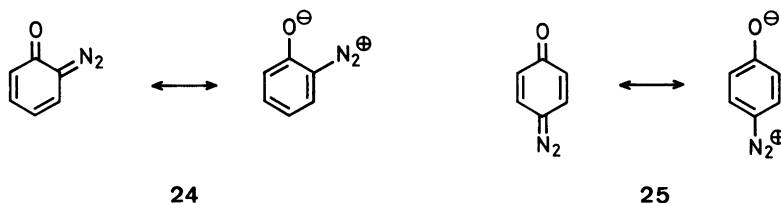
Indeed, X-ray data for 3,6-bis(diazo)-1,2,4,5-cyclohexanetetraone (**15**) (*22*) and 2,6-dichloro-1,4-benzoquinone-4-diazide (*49*) reveal shortened N—N distances as well as stretched C—N bonds, indicating a strong participation of the benzoid resonance structures according to the resonance in **24 and 25**; the corresponding values for benzenediazonium chloride are 138.5(9) pm for C—N and 109.7(6) pm for N—N (*60*). However, dipole moments (*61*) and N—N and C—O stretching frequencies in the IR spectra of a whole series of quinonediazides (*62–64a*) show clearly that the quinoid resonance forms contribute considerably more than the aromatic ones to the bond state of the molecule (Table 1.2).

The situation is not very clear for hetero-substituted diazoalkanes. Detailed statements are difficult to make, especially since, in the heavy-metal-substituted diazoacetates studied so far, experimental difficulties (decomposition of the crystals) and the dominating influence of the heavy atom cause very high standard deviations of the data. But some trends (see Table 1.1) are worth mentioning. (1) From the data for diazophenyl(triphenylsilyl)methane, especially the C—Si and C—N bond lengths, no indication for electron transfer from the diazo carbon to silicon (p_π–d_π backbonding as in **26**) can be found. (2) Shortening of the C—N bond and elongation of the N—N bond indicate in most cases a high contribution of the "cumulene" resonance structgure **18b** to the bond state of the diazo group. The only exception is bis(ethyl diazoacetate)mercury. The effect is most pronounced
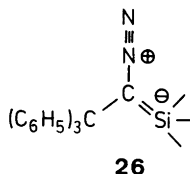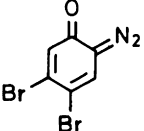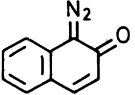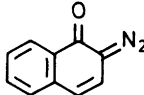

26
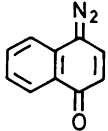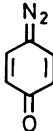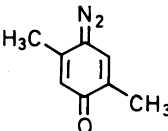
TABLE 1.2 Dipole Moments (*61*) and Diazo and Carbonyl Valence Frequencies of *o*- and *p*-Quinonediazides[a]

	4,5-Dibromo-1,2-benzoquinone-1-diazide	1,2-Naphtho-quinone-1-diazide	1,2-Naphtho-quinone-2-diazide	1,4-Naphtho-quinone-1-diazide	1,4-Benzoquinone-1-diazide	2,5-Dimethyl-1,4-benzoquinone-1-diazide
μ in benzene (D)	2.9	4.0	3.5	4.2	5.0	—
ν_{CN_2} (cm^{-1})[b]	2110	2173	2148	2014	—	2105
ν_{CO} (cm^{-1})[b]	1582	1618	1610, 1618	1618	—	1610

[a] From refs. 62–64.

[b] For comparison $\nu_{(CN_2)} = 2296$ cm^{-1} in benzenediazonium tetrafluoroborate; $\nu_{(CO)} = 1665$–1678 cm^{-1} for the parent quinones.

for ethyl [chlorobis(triphenylphosphine)palladium]diazoacetate, which is, by the way, the only known complex of a diazoalkane C-bonded to a Group VIII transition metal. The shift of $v(CN_2)$ in the IR spectrum to lower wave-numbers confirms this interpretation, although other influences, such as effective mass of the metal, could be main contributors to this effect (see Section 5.2).

Another interesting compound is diazobis(dimethylthallio)methane, $[(CH_3)_2Tl]_2CN_2$, which is an ionic compound, according to Raman and IR spectra, and has a linear $CN_2{}^{2-}$ group. This is in agreement with the fact that the thallium compound fails to undergo the characteristic reactions of other metal-substituted diazoalkanes, like phosphazine formation or cycloaddition to acetylenedicarboxylates (65).

1.3　Cis–Trans Isomerism of the α-Diazocarbonyl Compounds

A carbonyl group adjacent to the diazo group allows the incorporation of the CO function into a delocalized π-electron system as represented by ①. In regard to the constitution, two possibilities must be considered: a diazo–iso-diazo tautomerism ② similar to the one that is observed for diazomethane on treatment with base, and a diazoketone–diazoketole tautomerism ③. Prerequisite for both is the presence of a H atom at the diazo carbon.
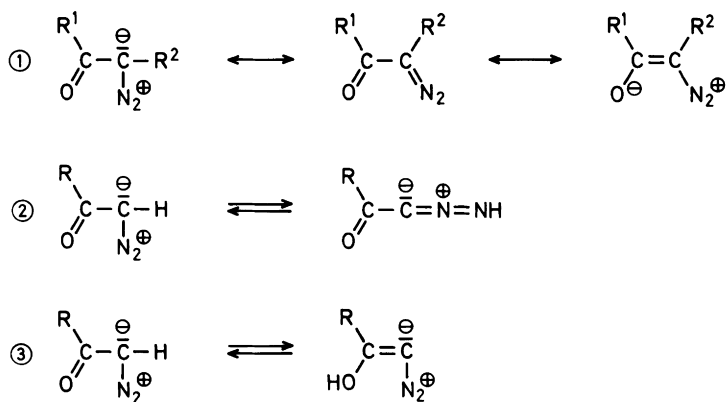
The inclusion of the carbonyl group into the mesomeric π bond system as indicated in ① will add partial double bond character to the CO—CN bond. This should result in hindered rotation about this bond and in the most favorable case should make it possible to detect s-cis and s-trans isomers. All atoms that are part of the resonance system ideally lie in one plane. The π_x orbital (Fig. 1.4) is delocalized over the whole system, whereas the π_y orbital is localized between both nitrogen atoms; the diazo carbon is sp^2 hybridized.
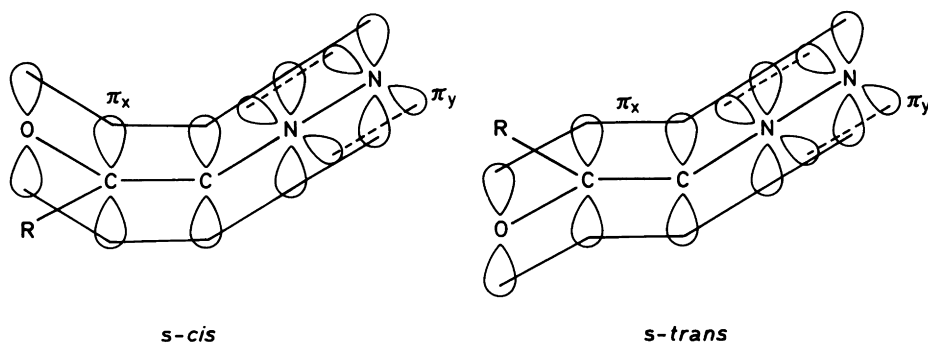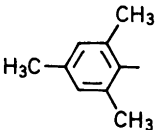
Fig. 1.4. Distribution of π electrons in cis- and trans-α-diazocarbonyl compounds.

The X-ray data (see Table 1.1) confirm this view of the bond state of α-diazocarbonyl compounds. All three resonance structures in ① contribute to the bond state. Surprisingly, the C—O distance is the same as in aliphatic ketones; one should realize, however, that this bond is generally not affected much by conjugation.

Cis-trans isomerism ① of numerous α-diazocarbonyl compounds has been studied by dynamic ^{1}H- (66–69), 13_{C-} (67a), and, for ethyldiazoacetate (70), ^{15}N-NMR spectroscopy. For all equilibria so far observed, the exchange process at room temperature is fast on the NMR time scale, but the spectra of the two isomers become observable at low temperatures. The Z/E isomer ratio is barely temperature-dependent, one exception being diazoacetyl chloride (67b). An argument against tautomerism ② or ③ is the fact that the ^{13}C-^{1}H coupling constant of the methine proton is the same in the spectra at fast exchange as in the spectrum of the isomer that dominates at low temperature (66). A compilation of rotational barriers in monosubstituted α-diazocarbonyl compounds is given in Table 1.3. Values for disubstituted α-diazocarbonyl compounds were found to be in the same range (67a). As can be seen from the table, the activation energy for Z-E isomerism is about 65–76 kJ mol^{-1} for α-diazoketones (**27b,c,g**), but only 38–52 kJ mol^{-1} for diazoacetates **27d** and **27e**. Probably the ester resonance reduces the C—C double bond character and with this the rotational activation barrier.

The NMR studies have shown that in solution monosubstituted diazoketones prefer the Z form, and disubstituted open-chain diazocarbonyl compounds exist exclusively (azibenzil, 2-diazopropiophenone) or preferentially (3-diazo-2-butanone, 3-diazo-4-heptanone, 1-diazo-1-phenyl-2-propanone, 2,4,6-substituted azibenzils) in the E form. In the crystalline state, the Z configuration is found for 1,4-bis(diazo)-2,3-butanedione (44) and p-bromo-ω-diazoacetophenone (71), and the E configuration is found for azibenzil (44a); in all three cases, configuration in solution and in the crystal

TABLE 1.3 Rotational Barriers and E/Z Isomer Ratios of α-Diazocarbonyl Compounds of the Type R—CO—CHN$_2$ (27)[a]

	R		$\Delta G^{\ddagger}_{298}$ for $(Z) \to (E)$[b]		E_a for $(Z) \to (E)$[b]		$(E)/(Z)$ ratio[c]	Ref.
			kJ mol^{-1}	kcal mol^{-1}	kJ mol^{-1}	kcal mol^{-1}		
a	H	1-Diazo-2-ethanone (diazoacetaldehyde)	66.5	15.9	—	—	0.449 (253)	66,67a
b	H$_3$C	1-Diazo-2-propanone (diazoacetone)	64.5	15.4	64.9	15.5	0.082 (233)	66
c	H$_5$C$_6$—CH$_2$	1-Diazo-3-phenyl-2-propanone	64.1	15.3	76.2	18.2	0.040 (233)	66
d	H$_3$CO	Methyl diazoacetate	53.6	12.8	52.3	12.5	0.859 (223)	66
e	H$_5$C$_2$O	Ethyl diazoacetate			37.7	9.0	0.840 (223)	66
f	H$_5$C$_6$	2-Diazo-1-phenyl-1-ethanone (ω-diazoacetophenone)	—	—	—	—	<0.02 (173)[d]	67
g	(mesityl structure)	2-Diazo-1-mesityl-1-ethanone	62.9[e]	15.0[e]	65.7[e]	15.7[e]	0.32 (173)	67
h	Cl	Diazoacetylchloride	f		f			67b

[a] Derived from temperature-dependent ^{1}H—NMR data in CDCl$_3$.
[b] Error limits are about $\pm$ 2.5 to 4.0 kJ mol^{-1}.
[c] At the temperature (K) given in parentheses.
[d] In CD$_2$Cl$_2$; the concentration of the E isomer is below the detection limit.
[e] For $E \to Z$.
f No Z/E assignment of the two isomers was made. $\Delta G^{\ddagger}_{298}$ values of 66.7 and 65.7 kJ mol^{-1} are found for the mutual interconversion of the two isomers.