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# The Structure of Aliphatic Diazo-compounds and Their Isomers

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The review describes the modern concepts concerning the electronic fine structure of aliphatic diazo-compounds based on experimental data (from infrared, ultraviolet, and PMR spectroscopy) and also quantum-mechanical calculations by the LCAO-MO method. These concepts explain many chemical properties of diazoalkanes and sometimes make it possible to predict them. Apart from "classical" aliphatic diazo-compounds, the structures and properties of the isomers—linear (*N*-isocyanamine) and cyclic (diazirines)—are considered.
The bibliography comprises 99 references.

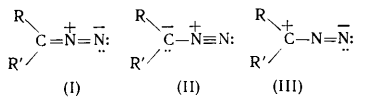
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## I. INTRODUCTION

About ten years have elapsed since the publication of extensive reviews [1] and monographs [2,3] on the structure and properties of diazoalkanes. During this period many papers have appeared on the fine structure of aliphatic diazo-compounds and their isomers. In the present review an attempt is made to give a general account of these new data, which are important for theoretical organic chemistry. The literature up to 1969 inclusive has been compiled.

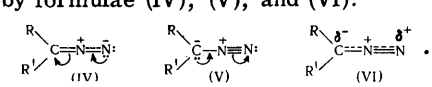
The problem of the structure of aliphatic diazo-compounds arose soon after their discovery by Curtius [4-10] in 1883. It was not until 50 years later that Boersch [11,12] demonstrated by physical methods and subsequently Clusius [13] by chemical methods the linear structure of diazo-compounds. In 1920–1930 it was suggested that the structure of diazoalkanes by represented by formulae (I), (II), and (III):[14-18]



(I) (II) (III)

Usually in the discussion of the structure of the $CN_2$ group of diazoalkanes in the ground state formulae (I) and (II) only are employed with the coordinate bonds N⇒N and C←N respectively. This is because formula (III) corresponds to a less stable molecular state compared with (I) and (II), since it contains fewer covalent bonds and the charges are removed to a greater distance [2].

The interatomic distances in diazomethane measured by Boersch by electron diffraction are inconsistent with the values calculated for these formulae on the basis of the additivity of the covalent radii even after correction for the atomic charges [19,20]. The experimental interatomic distances are intermediate between the values calculated for structures (I) and (II). This deviation is explained by the equalisation of electron density in the CN and NN bonds. The CN and NN bonds are non-integral: the CN bond is intermediate between a double and a single bond and the NN bond is intermediate between a double and triple bond. The negative charge of the $CN_2$ group is in fact distributed between the $\alpha$-carbon and $\beta$-nitrogen atoms, which can be expressed by formulae (IV), (V), and (VI):[2]



(IV) (V) (VI)

The most correct representation of diazoalkanes is by a combination of the limiting formulae (I) and (II) each making a definite contribution to the resonance hybrid. However, partly because these contributions are not known and partly for the sake of simplicity, only one of them is employed. Formulae (IV)–(VI) are somewhat more rigorous.

Some data on the distribution of electron density in diazoalkane molecules can be derived by studying their chemical properties. In many reactions diazoalkanes exhibit nucleophilic properties, since the carbon and the $\beta$-nitrogen atoms of the $CN_2$ group are negatively charged and the positively charged $\alpha$-nitrogen atom has already formed the maximum number of covalent bonds and cannot serve as a source of electrophilic activity [2].

It follows from the above considerations that the nucleophilic properties of diazoalkanes become weaker on introduction of electron-accepting substituents (for example, carbonyl or alkoxycarbonyl groups) and the thermal stability and the resistance to acids of diazo-compounds increase, while the introduction of electron-donating substituents (for example alkyl groups) make diazoalkanes more nucleophilic, reducing their stability at the same time. These problems are described in detail in Huisgen's review [1] and the monographs of D'yakonov [2] and Zollinger [3].

A more thorough study of the fine structure of diazoalkanes and the elucidation of the problem of the distribution of electron density in aliphatic diazo-compounds became possible only as a result of the application of spectroscopic and quantum-mechanical research methods.

## II. ELECTRONIC FINE STRUCTURE OF ALIPHATIC DIAZO-COMPOUNDS

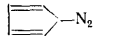
### 1. Diazohydrocarbons and Diazocarbonyl Compounds (Structural Studies by Spectroscopic Methods)

In structures (I) and (II) different electron densities arise at the $\alpha$-carbon atom and in substituents R and R′, to that the chemical shifts of the protons at the $\alpha$-carbon atom or in its substituents are then different depending on which particular form predominates. It is to be expected that the greater is the contribution of structure (II), i.e. the greater the negative charge at the $\alpha$-carbon atom, the

greater will be the chemical shift of the protons (on the $\tau$ scale) and conversely.

In 1964 Ledwith and Friedrich[21] measured the PMR spectra of a series of diazo-compounds and interpreted the results. Table 1 lists the chemical shifts of the protons at the $\alpha$-, $\beta$-, and $\gamma$-carbon atoms and the protons in the aromatic rings of the substituents. The results show that the chemical shift of the protons in diazomethane is much greater than in allenes, olefins, and aldehydes[21], which suggests a higher degree of screenings of the methylene protons and consequently a greater contribution of the carbanion structure (II) compared with structure (I).

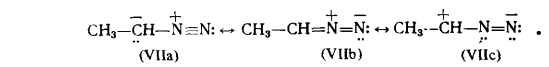
Table 1. Chemical shifts of the protons in diazoalkanes.

| Diazo-compound | Chemical shift of protons on $\tau$ scale, p.p.m* | Multiplicity of signal |
|---|---|---|
| $CH_2N_2$ | $\alpha$ 6.92 | |
| $CH_3CHN_2$ | $\alpha$ 6.78<br>$\beta$ 8.30 | doublet |
| $CH_2{=}CH{-}CHN_2$ | $\alpha$ 5.42<br>$\beta$ 6.71<br>$\gamma$ 8.93 | multiplet<br>quartet<br>triplet |
| $C_2H_5OOCCHN_2$ | $\alpha$ 5.04 | |
| $CH_3OOCCHN_2$ | $\alpha$ 5.04 | |
|  | $\alpha$ 3.38<br>$\beta$ 4.14 | quartet<br>quartet |
| $PhCHN_2$ | $\alpha$ 5.42<br>Ar 3.10 | multiplet |
| $Ph_2CN_2$ | Ar 2.74 | singlet |

*The operating frequency was 40 MHz and the following solvents were employed: carbon tetrachloride, methylene chloride, and trichlorotrifluoroethane. The effect of the solvent on the chemical shift is slight.

Koster[22], who made a thorough study of the PMR spectra of diazomethane in various solvents, holds similar views. However, one cannot exclude the possibility that such increase in the screening of $\alpha$-protons in diazomethane and its alkyl-substituted derivatives can be partly accounted for also by the diamagnetic anisotropy of the diazo-group, as happens in acetylenes and nitriles[23,24].

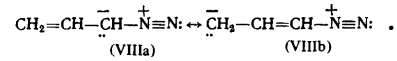
The chemical shift of the $\alpha$-protons of diazoethane is similar to that of the protons in diazomethane and therefore diazoethane is best described by formula (VIIa):



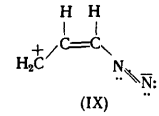
(VIIa) (VIIb) (VIIc)

One of the limiting structures (VIIc) is probably not achieved at all, since any appreciable contribution by this formula to the resonance hybrid would result in descreening of the $\beta$-protons, while their experimental chemical shift has the normal value for a methyl group joined to an unsaturated system.

Among all the protons of vinyldiazomethane, the greatest chemical shift ($\tau$ = 8.93 p.p.m.) corresponds to the protons at the $\gamma$-carbon atom. This finding is analogous to the increase of the screening of the carbanion methylene protons in allylmagnesium halides[25-27]:



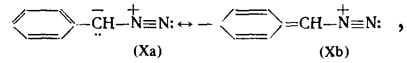
(VIIIa) (VIIIb)



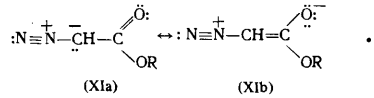
(IX)

The relative chemical shifts of the $\alpha$-, $\beta$-, and $\gamma$-protons might lead to the conclusion that structure (VIIIb), in which there is the greatest negative charge at the $\gamma$-carbon atom, makes the most appreciable contribution to the real state of the molecule. However, this kind of interpretation of the PMR spectra of vinyldiazomethane must be treated with caution, since such appreciable screening of the $\gamma$-methylene protons is possible also when vinyldiazomethane exists in the *cis*-form (IX); it is then postulated that the screening effect of the NN bond is similar to that of the C=C and C=O bonds[28].

The chemical shifts of the $\alpha$-protons of phenyldiazomethane and diazoacetic ester also indicate a greater contribution by the carbanion structure (II) compared with structure (I); the carbanion forms (Xa) and (XIa) of these diazo-compounds can be additionally stabilised by the transfer of the negative charge from the $\alpha$-carbon atom to the phenyl or alkoxycarbonyl group [structures (Xb) and (XIb)].

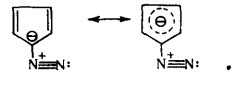


(Xa) (Xb)



(XIa) (XIb)

In diazocyclopentadiene the chemical shift of the $\beta$-ring proton is similar to the shift of the proton in cyclopentadienyl-lithium, which suggests that diazocyclopentadiene (XII) has almost entirely the carbanionic structure in the ring which thus has the properties of a non-benzenoid aromatic system[29,30]†.



(XIIa) (XIIb)

Thus the carbanionic and nucleophilic nature of diazoalkanes, which is assessed on the basis of their chemical properties, are consistent with qualitative PMR spectroscopic data.

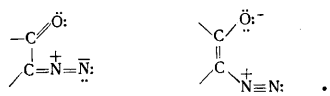
It must be emphasised that the terms "carbanionic" nature and "carbanionic" structure should not be understood solely as implying the transfer of the negative charge of the $CN_2$ group to the $\alpha$-carbon atom (which can in fact occur only in diazomethane). They should be understood in a wider sense as the transfer of a major fraction of the negative charge to the $\alpha$-carbon atom and to the substituents linked to it, which in fact occurs in all diazomethane derivatives

†Another aliphatic diazo-compound, which is also representative of a non-benzenoid aromatic system—diazocyclononatetraene—has been recently reported[31]. Its properties are being investigated.

It follows from the above that the PMR spectroscopic method is used mainly to investigate the electronic structure of diazo-compounds with hydrogen atoms or hydrocarbon groups linked directly to the $\alpha$-carbon atom. On the other hand, the interpretation of PMR spectroscopic data for $\alpha$-diazocarbonyl and particularly $\alpha$-diazo-$\beta\beta'$-dicarbonyl compounds is difficult and therefore infrared spectroscopy is widely employed to investigate the structures of these diazo-compounds.

$\alpha$-Diazocarbonyl and $\alpha$-diazo-$\beta\beta'$-dicarbonyl compounds occupy a somewhat special place among aliphatic diazo-compounds. They have a number of unusual properties for diazoalkanes: high resistance to the action of acids and heat, the absence of characteristic carbonyl reactions in many cases, and the capacity of individual compounds to form derivatives similar in type to aromatic diazonium salts [32].

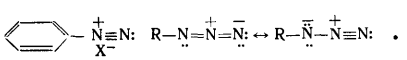
Two limiting structures have been proposed for aliphatic diazocarbonyl compounds, for which the terms "diazo-oxide" (XIIIa) and "diazoanhydride" (XIIIb) have become established in the literature [32]:



(XIIIa) (XIIIb)

The contributions by these structures to the resonance hybrid are estimated on the hypothesis that the transition from structure (XIIIa) to (XIIIb) will entail corresponding changes in the infrared spectrum. In consequence of the decrease of the double bond character in the carbonyl group, a shift of the absorption band to the long-wavelength region compared with the usual frequency for the keto- (or alkoxycarbonyl) group is to be expected. In the diazo-group there will be a change from a system of cumulative bonds in (XIIIa) to the NN triple bond of the diazonium structure in (XIIIb), which should give rise in the infrared spectrum to a shift of the absorption band associated with the NN stretching vibrations towards shorter wavelengths compared with diazohydrocarbons. These shifts of the absorption bands due to CO and NN stretching vibrations in fact characterise the contributions by structures (XIIIa) and (XIIIb) to the real state of the molecule [32-37].

In order to discover the region in which the absorption bands of the diazo-group in diazocarbonyl compounds may be located, we shall consider the aromatic diazonium salts (XIV) and the azides (XV):



(XIV) (XV)

The real state of diazonium salts can be quite justifiably expressed by structure (XIV), the diazo-group absorbing in the region 2200–2300 $cm^{-1}$; on the other hand, the absorption by azides (XV), where the contributions by both structures are approximately equal, is observed in the region 2100–2160 $cm^{-1}$. [38,39]

Thus the diazo-group in diazocarbonyl compounds should absorb in the region 2000–2300 $cm^{-1}$. The greater is the shift within these limits towards higher frequencies, the greater is the contribution by structure (XIIIb) to the resonance hybrid, and the greater is the shift towards lower frequencies, the greater is the contribution by structure (XIIIa) (Table 2).

Naturally, the contribution by the diazoanhydride structure is particularly large in those compounds where the transition to the diazo-oxide form is impossible for some reason; an example of this is 5-diazouracil ($\nu_{N_2}$ = 2190 $cm^{-1}$). [32]

Absorption by the CO groups in diazocarbonyl compounds is to be expected in the region between 1720 $cm^{-1}$ (absorption by the carbonyl group in ordinary ketones) and 1600 $cm^{-1}$ (absorption by the carbonyl group in enolised $\beta$-dicarbonyl compounds with an intramolecular hydrogen bond) [32]. The greater is the shift towards lower frequencies, the greater is the contribution of the CO group to the formation of structure (XIIIb) and conversely (Table 3).

**Table 2.** The colour of aliphatic diazo-compounds and the frequencies of the absorption bands due to the diazo-group [32-37,40-42].

| Diazo-compound | $\nu_{N_2}$, $cm^{-1}$ | Colour |
|---|---|---|
| Cyclic diazodicarbonyl compounds | 2150–2190 | colourless |
| R'-CO-$CN_2$-CO-R | 2140–2160 | colourless, yellow |
| R-CO-$CN_2$-R' (linear and cyclic) | 2080–2130 | greenish-yellow |
| Diazohydrocarbons | 2020–2120 | greenish-yellow, red |

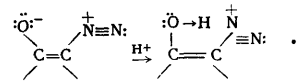
It was found [33,34] that not only the magnitude of the shift of the absorption band of the NN stretching vibrations but also the molar integral absorption corresponding to this band may serve as a criterion of the involvement of the limiting forms (XIIIa) and (XIIIb) in the resonance hybrid. The greater is the contribution by the diazoanhydride form (XIIIb) and therefore the greater is the high-frequency shift of the NN stretching vibration band, the lower is the molar integral absorption corresponding to this band. For example, for diazodicarbonyl compounds with an enhanced contribution of the diazoanhydride form, it is smaller by a factor of 1.5–2 than for diazomonocarbonyl compounds, amounting to (3.2–4.1) $\times 10^{-4}$ litre $mole^{-1}$ $cm^{-1}$ for the former and (4.6–5.2) $\times 10^{-4}$ litre $mole^{-1}$ $cm^{-1}$ for the latter [33-35].

**Table 3.** Absorption by the CO group in carbonyl and diazocarbonyl compounds [32].

| Diazocarbonyl compound | $\nu_{C=O}$ in diazocarbonyl compounds, $cm^{-1}$ | $\nu_{C=O}$ in carbonyl compounds, $cm^{-1}$ |
|---|---|---|
| R—$CN_2$—CO—R' | 1640—1670 | 1705—1725 |
| R—$CN_2$—COOR' | 1670—1720 | 1735—1750 |
| R—$CN_2$—$CH_2$—COOR' | 1735—1750 | 1735—1750 |
| H—$CN_2$—CO—R' | 1620—1630 | 1705—1725 |
| H—$CN_2$—COOR' | 1690 | 1735—1750 |

The structure of diazocarbonyl compounds approaches more closely the diazonium structure the greater is the number of carbonyl groups adjacent to the diazo-group. Then in the series of aliphatic diazo-compounds there is an increase in stability; thus diazoketones, which usually have a yellow or a greenish-yellow colour, are decomposed slowly by acetic and benzoic acids and fairly rapidly by inorganic acids. Diazodicarbonyl compounds are much

more resistant to the action of acids. They can be frequently dissolved in concentrated sulphuric acid and be isolated unchanged on dilution with water. They are decomposed by concentrated acids only on heating. The explanation is that in diazodicarbonyl compounds, where the structure (XIIIb) makes a particularly large contribution, the proton is attached to the strongly electronegative oxygen atom and not to the $\alpha$-carbon atom [form (XIIIa)] with formation of an unstable diazonium ion:



For this reason, the greater is the contribution by structure (XIIIb), the more resistant is the diazocarbonyl compound to the action of acids [32].

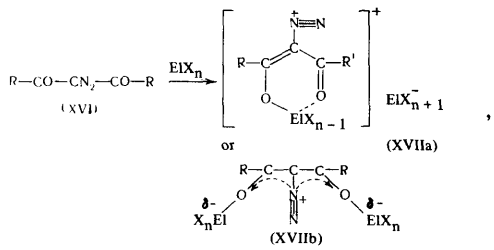
All the findings described above hold also for $\alpha$-diazocarbonyl compounds; the carbonyl group in the $\beta$-position relative to the diazo-group makes no contribution to the formation of the diazoanhydride structure (Table 3). The contribution by structure (XIIIb) to the real state of the molecule increases when electron-accepting substituents (halogens and carbonyl or alkoxycarbonyl groups) are present next to the carbonyl or diazo-groups and decreases on introduction of electron-donating groups (for example, alkyl groups), which is confirmed by the spectroscopic and chemical properties in the series of diazocarbonyl compounds [33-35].

The decrease of the quantum yield of the photolysis of diazocompounds on passing from diazohydrocarbons to diazocarbonyl compounds is also explained by the increased contribution of the more stable diazonium structure (XIIIb) [43] (Table 4).

Table 4. Quantum yields of the photolysis of diazo-compounds [43].

| Diazo-compound | Quantum yield |
|---|---|
| $Ph_2CN_2$ | 0.78 |
| $C_5H_5OOCCHN_2$ | 0.66 |
| $PhCOCHN_2$ | 0.46 |
| $(PhCO)_2CN_2$ | 0.31 |
| $p$-$(N_2CHCO)_2C_6H_4$ | 0.15 |

There exist also derivatives of aliphatic diazo-compounds whose structure is very close to that of diazonium salts; these are adducts of diazodicarbonyl compounds with Lewis acids—(XVIIa) or (XVIIb):[44-48]



where $ElX_n$ is a Lewis acid.

Colourless crystalline compounds are formed as a result of the addition of the Lewis acid to the oxygen atom, which entails additional withdrawal of the negative charge from the carbon atom of the $CH_2$ group and the structure acquires the properties of an aromatic diazonium salt. This is indicated by the shift of the absorption band of the diazo-group of the adduct to the region 2180–2140 $cm^{-1}$ relative to the absorption by the initial diazodicarbonyl compounds (XVI) (2130–2150 $cm^{-1}$).

Thus $\alpha$-diazocarbonyl and particularly $\alpha$-diazo-$\beta\beta'$-dicarbonyl compounds are intermediate as regards their chemical properties and spectroscopic characteristics between diazohydrocarbons and aromatic diazonium salts. A group of very interesting compounds—$o$- and $p$-quinone diazides and $p$-iminoquinone diazides [49], the discussion of which is outside the scope of the present review—also belong to this class.

The spectroscopic characteristics of aliphatic diazo-compounds examined in this section suggest with a fair degree of certainty that either the carbanion form or the diazoanhydride form similar to it (in the case of diazo-carbonyl compounds) make the greatest contribution to the real state of these compounds. However, it must be emphasised that these conclusions are purely qualitative, whereas for some time now it has been necessary to examine the structures of diazo-compounds also on a quantitative basis‡.

## 2. LCAO-MO Calculations for Aliphatic Diazo-compounds

Calculations on the $\pi$-electron structure of diazoalkanes by the LCAO-MO method have been carried out by Schuster and Polansky [50] and by Simon and Badilescu [51]. They found the values of $\pi$-electron energy, delocalisation energy, the bond orders, and atomic charges. On this basis, attempts were made to establish to what extent the calculated data agree with experiment and what additional information about the structure and properties of aliphatic diazo-compounds may be obtained with their aid.

The delocalisation ($E_D$) and combination ($E_C$) energies of diazoalkanes may be used as criteria of their relative resistance to the action of acids and heat [50]. The combination energy is regarded as the energy contribution when diazo-compounds are formed from the $\pi$-electron system of the $CN_2$ group and the $\pi$-electron systems of the substituents. Table 5 lists the values of $E_D$ and $E_C$ for a number of diazoalkanes. It shows that, with decrease if the resistance to the action of acids and heat in the series diazomethane, diazoethane, and dimethyldiazomethane [2], there is a parallel decrease of the $E_D$ values for these compounds. However, on passing from diazomethane and its alkyl-substituted derivatives to diazoalkanes, where the substituents exhibit a conjugation as well as an inductive effect, $E_D$ ceases to be a good criterion of the stability of diazo-compounds, becoming inconsistent with experimental data.

In order to account for the difference in the resistance of these diazoalkanes to the action of acids, it is best to

‡For a quantitative estimation of the contributions by the diazonium and diazohydrocarbon structures to the resonance hybrid of diazo-compounds, Fahr attempted to employ the difference between the frequencies of the NN stretching vibrations of the diazo-group and molecular nitrogen ($\gamma_{NN}$ = 2331 $cm^{-1}$): the smaller the difference the closer is the structure to the diazonium form and conversely the greater the difference the closer is the structure to the diazohydrocarbon form. There are corresponding changes also in the chemical properties of the compounds (private communication).

employ the values of $E_C$: the increase of the resistance of diazo-compounds to acids in most cases agrees with the increase of their $E_C$ values. Table 5 shows that only diphenyldiazomethane, which is in fact more stable than phenyldiazomethane, deviates from this series. The authors explain this by the fact that the angle of rotation of both phenyl groups relative to the plane of the diazo-group was chosen arbitrarily to facilitate the calculation.

**Table 5.** Delocalisation energies ($E_D$), combination energies ($E_C$), and the losses of the delocalisation energy ($E_D^* - E_D$) of diazoalkanes[50,51].

| Diazo-compound | $E_D$, $\beta$ | $E_C$, $\beta$ | $\lvert E_D^* - E_D \rvert$, $\beta$ |
|---|---|---|---|
| $CH_2N_2$ | 0.7674 | — | 1.8946 |
| $CH_3CHN_2$ | 0.6981 | — | — |
| $(CH_3)_2CN_2$ | 0.6588 | — | — |
| $C_2H_5OOCCHN_2$ | 1.5702 | 0.5106 | 1.207 |
| $CH_3COCHN_2$ | 1.4284 | 0.5406 | — |
| $PhCOCHN_2$ | | | 1.1458 |
| $PhCHN_2$ | 3.3298 | 0.6240 | — |
| $Ph_2CN_2$ | 5.3193 | 0.5519 | 1.1160 |
| $(C_2H_5O_2C)_2CN_2$ | 2.3154 | 1.5480 | — |
| $N_2CHCO-(CH_2)_2-COCHN_2$ | | | 1.1190 |
| Diazofluorene | 6.3709 | 1.2201 | — |
| Diazocyclopentadiene | 2.8653 | 1.6258 | — |

If one remembers that diazoalkanes are nucleophilic agents whose reactivity should be determined to a first approximation by the localisation of the negative charge in the $CH_2$ group (without taking into account steric and certain other factors), then we should have the following general tendency: a decrease of the reactivity of diazoalkanes with increasing $E_D$ and $E_C$. In fact in the series of diazomethane and its alkyl-substituted derivatives the increase of nucleophilic activity is accompanied by a decrease of $E_D$; there is a similar decrease of $E_C$ in the series of diazo-compounds whose substituents are conjugated with the diazo-group.

Another criterion of the reactivity of diazo-compounds, proposed by Simon[51], is the loss of delocalisation energy ($E_D^* - E_D$). Its value characterises the decrease of $E_D$ on transition from the ground state of the molecule to the activated complex in which the conjugation is weakened at the CN bond to be dissociated. It is believed[51] that $E_D^* - E_D$ can be usefully employed only to characterise adiabatic reactions, i.e. reactions in which the radical formed is in a singlet state. On the other hand, when the reaction is non-adiabatic, i.e. there is a change in electron spin in the activated complex with subsequent formation of a triplet ground state, this criterion is no longer valid.

Table 5 lists the values of $E_D^* - E_D$; in general (with the exception of diazomethane) there is an increase of the thermal and photolytic stability of diazoalkanes with increase of $E_D^* - E_D$.

Schuster and Polansky[50] determined the $\pi$-electron contribution to the enthalpy of decomposition of diazonium cations ($\Delta H_\pi$) characterising the change in $\pi$-electron energy on passing from the diazonium cation to a carbanion cation and nitrogen: $RN_2^+ \rightarrow R^+ + N_2$. The results are presented in Table 6.

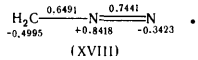
It is seen that the phenyldiazonium cation is more stable than the methyldiazonium cation to the extent of 0.63 $\beta$. Such quantum-mechanical examination of diazo-compounds permits the solution of many problems, in particular the problem of the structure of the simplest representative of this class—diazomethane.

The dipole moment of diazomethane ($\mu$ = 1.5 D) does not provide unambiguous information about the relative contributions of the two forms [(I) and (II)] to the real state of the molecule[52]. The dissociation energy of the CN bond in diazomethane found from mass-spectrometric data is low (1.9 eV)[53] and closer to the energy of a single than a double bond, i.e. this suggests that structure (II) predominates. The above results (p. 835) of the study of the PMR spectra of diazomethane also confirm its carbanionic structure.

**Table 6.**

| R | $CH_3$ | $C_6H_5$ | $p$-$(CH_3)_2N-C_6H_4$ |
|---|---|---|---|
| $\Delta H_\pi\beta$ | −0.2463 | +0.3831 | +0.4056 |

The molecular diagram (XVIII) of diazomethane calculated by Schuster and Polansky[50] also confirms the greater contribution by the carbanionic structure, as can be inferred from the negative charges at the $\alpha$-carbon and $\beta$-nitrogen atoms and the bond orders:

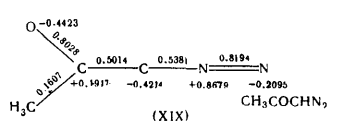



(XVIII)

The molecular diagrams of other diazo-compounds[50] also confirm their carbanionic structure, deduced experimentally in earlier studies, and agree well with qualitative data derived from their PMR spectra.

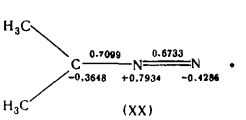
The PMR spectroscopic data suggested a transfer of part of the negative charge from the $\alpha$-carbon atom of the $CN_2$ group to the substituents linked to it. This assumption is consistent with the molecular diagrams of phenyl- and diphenyl-diazomethane, diazoacetic ester, and others, and also with their chemical behaviour (for example, in reactions with ketones and $\alpha$-diketones[54-58]).

The molecular diagrams of diazocarbonyl compounds likewise confirm that the diazoanhydride structure predominates to a considerable extent over the diazo-oxide structure, which is reflected in a transfer of the negative charge from the diazo-group to the carbonyl oxygen and an increase of the C–C bond order between the carbonyl and the diazo-group approximately to 1.5 units [see, for example, diagram (XIX)]:




(XIX)

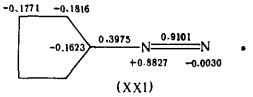
The calculated data show that only in dimethyldiazomethane, where the two methyl groups have a considerable $+I$ effect, the contribution of the carbanionic structure is somewhat less than that of the non-carbanionic structure (XX):




(XX)

In all the remaining cases the carbanionic form with delocalisation of the negative charge over the α-carbon atom and the substituents linked to it makes the major contribution.

Diazocyclopentadiene is known to be very stable; it does not enter into typical reactions of diazoalkanes, but is capable of electrophilic substitution. These properties are consistent with the high value of $E_C$; it follows from the molecular diagram (XXI),




(XXI)

that electrophilic substitution should take place preferentially in the 2- and 5-positions; however, the difference between the charges in these positions compared with the 3- and 4- positions is not very great. When diazocyclopentadiene is nitrated, α- and β-nitrodiazocyclopentadienes are formed in proportions of 3 : 2.

Until recently it was believed that the α-nitrogen atom in diazo-compounds transmits electron density but its own charge remains unchanged. The calculated data [50] show that this is probably not entirely true and the positive charge of the α-nitrogen atom changes, albeit not very greatly [see, for example, the molecular diagrams (XVIII)–(XXI)].

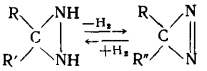
The data quoted show that the qualitative description of the structure of aliphatic diazo-compounds based on the study of the PMR and infrared spectra is confirmed quantitatively when quantum-mechanical computational methods are applied to diazo-compounds. Altogether the experimental and calculated data make it possible to describe accurately not only the fine structure of aliphatic diazo-compounds, which explains their behaviour in chemical reactions, but sometimes it is also possible to predict such behaviour.

## III. ISOMERS OF ALIPHATIC DIAZO-COMPOUNDS

### 1. Cyclic Isomers (Diazirines)

Cyclic isomers of diazoalkanes (diazirines) were discovered in 1960–1961 independently by Paulsen [59] and Schmitz and Ohme [60]. The discovery of this new class of compounds was highly unexpected, since in earlier investigations [7,61] cyclic structures were discussed as possible alternatives for aliphatic diazo-compounds, but it was never suggested that the cyclic isomers can exist as a separate class of compounds.

However, it was found that frequently it is easier to obtain the more stable cyclic isomers than the less stable linear diazo-compounds. The usual method of preparation of diazirines (XXIII) is by oxidising diaziridines (XXII):




(XXII) (XXIII)

The chemistry of diazirines is developing very rapidly and their structure was established a year after discovery. The synthesis, structure, and properties of diazirines have been described in detail in a monograph by Schmitz [62] and therefore here we shall consider them very briefly.

The bond lengths in diazirine were determined from its microwave spectra: 1.48 Å (C–N) and 1.23 Å (N–N). Its dipole moment is 1.59 D, i.e. very close to the dipole moment of diazomethane (see p. 838). [63–65]

The PMR spectrum of diazirine in carbon tetrachloride has a singlet at $\tau$ = 9.60 p.p.m. The signal of the protons at the ring carbon atom is located in a relatively high field, which indicates the presence of a strained three-membered ring [66].

The equivalence of both nitrogen atoms was demonstrated in pentamethylenediazirine as an example using a tracer atom method [67].

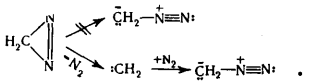
The ultraviolet spectra of diazirines have an absorption maximum at 340 nm, which is close to the absorption of azomethane ($\lambda_{max}$ = 343 nm) but differs sharply from the absorption by the isomeric compounds diazomethane ($\lambda_{max}$ = 412 nm) and *N*-isocyanamine ($\lambda_{max}$ = 247 nm). [68,69]

In the infrared spectra the absorption band of the azo-group at 1580–1600 $cm^{-1}$ is observed instead of the absorption band of the linear diazo-group in the region of 2000–2200 $cm^{-1}$.

The difference between the structures leads also to a sharp difference between the chemical properties; diazoalkanes are some of the most reactive substances known in organic chemistry, while diazirines are much more stable. Thus diazirine is more stable that diazomethane to the extent of 30 kcal $mole^{-1}$ (according to mass-spectrometric data, the heats of their formation are respectively 79 and 49 kcal $mole^{-1}$). [53,70–72] Aliphatic diazo-compounds are extremely sensitive to acids, while alkyl-substituted diazirines decompose only when treated with concentrated inorganic acids (80–90% sulphuric acid).

In almost all reactions of diazoalkanes new C–C bonds are formed, while in the case of diazirines Thiele's view that the N=N bond is more reactive is confirmed. For example, hydrogen and Grignard reagents readily add to the nitrogen–nitrogen double bond. However, there are also similarities between the reactions of these two classes of compounds: both diazoalkanes and diazirines decompose on photolysis and thermolysis with evolution of nitrogen and the formation of carbenes.

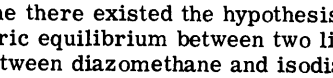
Diazirines can be converted into linear diazo-compounds: it has been shown by infrared spectroscopy that, when diazirine is irradiated in a solid nitrogen matrix at 20°K, diazomethane is formed [72]. Experiments using labelled nitrogen suggest that the mechanism involving the splitting off of molecular nitrogen and its subsequent addition to the carbene with formation of the linear diazomethane is more likely than the cleavage of the three-membered ring and direct formation of diazomethane:




It has also been shown [73] that diazomethane is formed in the photolysis of diazirine in the gas phase too. In the liquid phase the formation of the linear diazo-compound is observed in the photolysis of pentamethylenediazirine [74]. Studies dealing with the conversion of diazirines into linear diazo-compounds and designed to determine the mechanism of this process are being continued.

### 2. Linear Isomers (*N*-Isocyanamines)

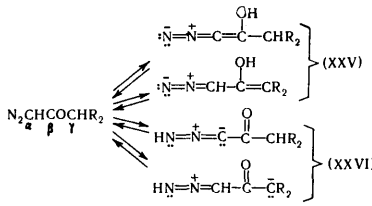
For a long time there existed the hypothesis of a possible tautomeric equilibrium between two linear structures, namely between diazomethane and isodiazomethane [75,76]:



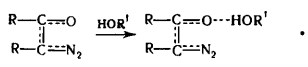

(XXIV)

Only in recent years, as a result of Koster's work[22] on the PMR spectra of diazomethane at different temperatures and a careful study of the infrared spectra of 12 diazomethane specimens prepared in different ways[77], was the absence of diazo–isodiazo tautomerism in diazomethane demonstrated.

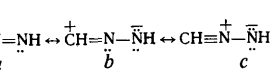
The absence of tautomerism in diazohydrocarbons did not allow an *a priori* rejection of such isomerism in diazocarbonyl compounds, where the mobility of the $\alpha$- and $\gamma$-hydrogen atoms should be enhanced owing to the influence of the carbonyl group. In this case two types of tautomerism could be postulated: keto–enol (XXV) and diazo–isodiazo (XXVI):[78]



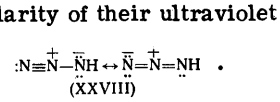

However, Fahr[79] made a detailed study in 1959 of the ultraviolet spectra of diazocarbonyl compounds and showed that the change in the spectroscopic characteristics of these substances on passing from hydrocarbon to hydroxylated solvents, which had been previously explained by a shift of the tautomeric equilibrium (XXV)–(XXVI), is in fact due to the formation of a hydrogen bond:



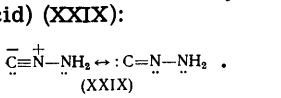
Thus it has now been rigorously demonstrated that there is no tautomerism in aliphatic diazo-compounds. However, there exists a linear isomer of diazomethane, discovered more than 30 years ago[80–82]. It was obtained by Müller[80–83] by the action of an aqueous solution of ammonium chloride on the compound formed by the reaction of diazomethane with methyl-lithium. Three limiting structures [(XXVIIa)–(XXVIIc)] were suggested for the very unstable compound (called "isodiazomethane") isolated after vacuum distillation of the solvent:


(XXVII)

Thus, on the basis of the electronic configuration, the isomeric diazomethane, whose properties differ appreciably from those of the usual diazomethane, was regarded[82] as an analogue of hydrazoic acid (XXVIII). This analogy was apparently confirmed by the instability of both compounds and the similarity of their ultraviolet spectra.

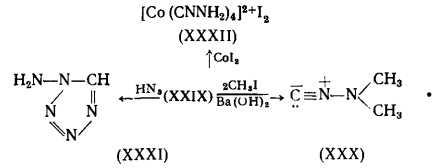

(XXVIII)

However, the latest studies have shown quite rigorously that "isodiazomethane" is in fact *N*-isocyanamine (the amide of fulminic acid) (XXIX):


(XXIX)

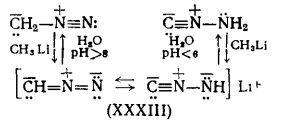
This structure of the isomeric diazomethane is also confirmed by infrared and PMR spectroscopic data[83]. The infrared spectrum of compound (XXIX), like that of cyanamide[84], contains absorption bands associated with the NH stretching vibrations (3170 and 3290 $cm^{-1}$) and deformation vibrations (1630 $cm^{-1}$) and also a weak absorption at 2130 $cm^{-1}$ attributed to the isonitrile group. The PMR spectrum of the isomeric diazomethane contains only one broad band ($\tau$ = 3.6 p.p.m.) which is not split when the temperature is sharply reduced and resembles in shape and position the corresponding signal from carboxylic acid amides ($\tau$ = 3.5–3.8 p.p.m.). The compound readily exchanges both hydrogen atoms for deuterium and under the action of alkali is rapidly converted into diazomethane. In the first case the signal in the PMR spectrum completely disappears and in the second it is replaced by the signal due to the protons in the diazomethane molecule ($\tau$ = 6.8 p.p.m.).[21]

The chemical reactions of the isomeric diazomethane are satisfactorily consistent with the spectroscopic data, confirming that its structure is (XXIX). Thus it proved possible to carry out a reaction involving the amino-group: *N*-isocyanodimethylamine (XXX), previously described in the literature, was obtained[85]:

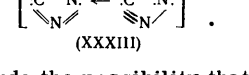



Like other isonitriles, *N*-isocyanamine readily forms the corresponding tetrazole (XXXI) by reaction with hydrazoic acid and complexes (XXXII) with cobalt and iron salt. Other reactions of compound (XXIX) characteristic of isonitriles have also been investigated[83,85–87]. Consequently both physical and chemical research methods fairly clearly demonstrate that the isomeric diazomethane is the first member of the series of *N*-isocyanoalkylamines and *N*-isocyanodialkylamines, which were described for the first time quite recently[88].

Compared with diazirine, *N*-isocyanamine shows somewhat greater similarity to diazomethane. This is shown by the instability of both isomers and by their capacity for ready interconversion, whereas diazomethane is not converted into diazirine. The diazomethane–fulminic acid amide interconversions do not take place directly but only via their deprotonated form—the diazomethyl anion (XXIII)—which is readily obtained by the action of methyl-lithium on diazomethane or its isomer (XXIX). On hydrolysis in an acid medium, diazomethyl-lithium forms the amide (XXIX) and on hydrolysis in an alkaline medium diazomethane is formed:


(XXXIII)

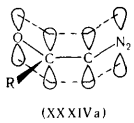
The tautomeric conversion of the anion is apparently facilitated by the hydrogen bond in the transition state (XXXIII):[83]


(XXXIII)

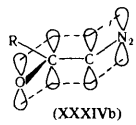
Nor can one exclude the possibility that the protonation of the diazomethyl anion involves the formation of isodiazomethane proper (XXIV), which is an extremely unstable intermediate in the transformation of diazomethane into *N*-isocyanamine (and conversely). However, this hypothesis requires rigorous tests.

3. *cis–trans*-Isomerism of Diazocarbonyl Compounds

It follows from the above (pp. 836–837) that whatever the contribution of structure (XIIIb) to the real state of the molecule of the diazocarbonyl compound, the C—C bond between the carbonyl and the $CN_2$ group will always exhibit a certain amount of double bond character. This should prevent free rotation about the C–C bond and consequently the existence of two forms of diazocarbonyl compounds may be expected: *cis*- [(XXXIVa)] and *trans*- [(XXXIVb)]. In this case the terms "*cis*" and "*trans*" refer to the relative positions of the $\pi$-electron clouds of the carbonyl group and diazo-group, while the group linked to the carbonyl is located in the *trans*-position relative to the diazo-group in the *cis*-form (and conversely):



(XXXIVa)
*cis*-



(XXXIVb)
*trans*-

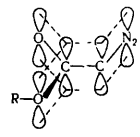
The hypothesis of conformational isomerism of $\alpha$-diazoketones was put forward by Pecile et al. [89] and later by Leveson and Thomas [90] to account for certain characteristics of their infrared and ultraviolet spectra. However, the evidence which they adduced in favour of this assumption was not sufficiently rigorous.

A decisive proof of the real existence of the conformational isomerism of $\alpha$-diazoketones was obtained by Kaplan and Melloy who investigated the PMR spectra of diazocarbonyl compounds (XXXV) at different temperatures [91–93]:

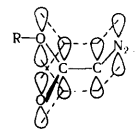
$RCOCHN_2$ (XXXV)
a. R=H; b. R=$CH_3$; c. R=$C_2H_5$; d. R= t-$C_4H_9$; e. R=Ph—$CH_2$; f. R=$CH_3O$; g. R=$C_2H_5O$; h. R=Ph; i. R=*p*-$NO_2$—$C_6H_4$.

They made the following observations: in the majority of the diazocarbonyl compounds investigated (XXXVa, b, c, e, f, g) the signal of the methylidyne proton is gradually broadened as the temperature is reduced and finally splits into two components. This type of change in the PMR spectra is characteristic of an equilibrium mixture of two substances: the average signal is observed at high rates of interconversion and two signals are observed at low rates. The constancy of the spin–spin coupling constant for the methylidyne proton ($J_{^{13}C-H}$) corresponding to the average signal and the signals of each of the substances undergoing conversion is evidence that any type of tautomerism involving the methylidyne proton is impossible. Consequently in this case only a *cis–trans* isomeric equilibrium can exist and the two peaks in the low-temperature spectra correspond to the *cis*- and *trans*-forms of the diazocarbonyl compound. On the basis of analogies in the literature [94,95], the signal in the stronger field was attributed to the *trans*-form, whence the ratio of the *cis*- and *trans*-conformers may be obtained from the ratio of the signal intensities.

Table 7 shows this ratio for the diazocarbonyl compounds (XXXV) investigated varies markedly as a function of the group R. The high content of the *cis*-conformer in compounds (XXXVb, c, e) compared with diazoacetaldehyde can probably be explained by the steric hindrance to the formation of the *trans*-forms of these diazocarbonyl compounds. In general, one may expect that the *cis/trans* ratio will increase as the steric requirements of the substituents become more stringent. However, this factor is not always decisive. Thus, on the basis of steric considerations, an appreciable predominance of the *cis*-form might have been expected in diazoacetic esters (XXXVf, g), but the *cis/trans* ratio is in fact only a little in excess of unity. This can probably be accounted for by the fact that the $\pi$-electron systems of both forms have the same geometry (XXXVIa, b), which leads to identical interactions: as a result, the difference between the free energies $\Delta F$ of the two conformers is insignificant.



(XXXVIa)



(XXXVIb)

**Table 7.** Compositions in, and activation energies $E_a$ for, the *cis–trans* interconversion of diazocarbonyl compounds [92].

| Compound | Fraction | | $E_a$, kcal mole$^{-1}$(°C) |
|---|---|---|---|
| | *cis* | *trans* | |
| (XXXVa) | 0.690 | 0.310 | |
| (XXXVb) | 0.924 | 0.076 | 15.5±0.9 (11.8) |
| (XXXVc) | 0.941 | 0.059 | 16.1±0.6 (6.5) |
| (XXXVd) | 0.990 | 0.010 | |
| (XXXVe) | 0.962 | 0.038 | 18.1±0.6 (1) |
| (XXXVf) | 0.538 | 0.462 | 12.5±0.9 (−25) |
| (XXXVg) | 0.540 | 0.460 | 9±0.8 (−32) |

For a number of compounds (XXXVd, h, i), only one signal is observed over the entire temperature range investigated. Among the explanations proposed for this experimental finding, the most acceptable is the hypothesis that all these diazoketones exist mainly in the *cis*-form owing to the strong steric interaction between the diazo-group and the bulky R radical in the *trans*-form.

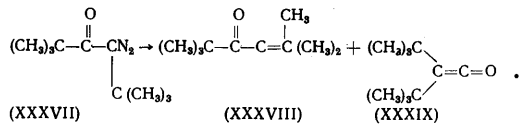
The activation energy $E_a$ which determines the barrier to free rotation, varies from 9 to 18 kcal mole$^{-1}$ (Table 7)§. Comparison of the values of $E_a$ and the orders of the central C–C bond [50] shows that a decrease of the double bond character of this linkage lowers the barrier to free rotation.

The existence of diazoketones in the *cis*- and *trans*-forms can be used to explain some of their reactions (in particular, their decomposition processes); it is then of course necessary to take into account the relative rates of the reaction and of the *cis–trans* transition. Naturally, the possibility of the formation of the reaction products from the preferred conformation must be considered only when the rate of interconversion of the two forms is lower than the rate of the decomposition reaction.

Assuming that the formation of ketens in the Wolff rearrangement takes place as a concerted synchronous process [97] and only via the *cis*-form of the diazoketone, which is the most favourable for this purpose, Kaplan and Melloy made a fairly successful attempt to account for the results of certain reactions of $\alpha$-diazoketones [92,98,99].

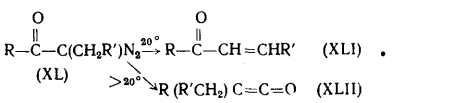
§$E_a$ for the interconversion of the *cis*- and *trans*-conformers of diazoacetone was recently calculated [96] by Hückel's molecular orbital method. The calculated value (about 14 kcal mole$^{-1}$) agrees well with the experimental activation energy found by Kaplan and Melloy (Table 7).

Thus, owing to the powerful repulsion of the two t-butyl groups, the diazoketone (XXXVII) cannot exist in the *cis*-form and therefore its photolytic, thermal, and catalytic decomposition results in the formation of compound (XXXVIII) and only traces of the keten (XXXIX):



(XXXVII) (XXXVIII) (XXXIX)

At low temperatures the diazoketones (XL) also exist mainly as the *trans*-conformers. However, the formation of the *cis*-form is less sterically hindered and on raising the temperature the energy received by the molecules is apparently sufficient for the formation of appreciable amounts of the *cis*-conformer. For this reason, the photolytic and catalytic decomposition of diazoketones (XL) at 20°C leads mainly to compounds (XLI). At higher temperatures the ketens (XLII) are mainly obtained:



(XL) (XLI) (XLII)

Thus the study of the conformational isomerism of diazoketones, which is itself of considerable theoretical interest, will undoubtedly prove useful also for a better understanding of the mechanism of the reactions of this class of compounds.

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