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DIPOLE MOMENTS AND MOLECULAR CONFORMATION IN ALIPHATIC DIAZOKETONES*

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Abstract—The dipole moments of diazoacetone $RCOCHN_2$ and its three chloro derivatives substituted at the alkyl group have been determined. The experimental values are consistent with a rigid planar structure of the $COCHN_2$, where the CO and CN_2 groups may be either in *cis* or *trans* configuration In the parent molecule, an equilibrium is operative between the two and in the halogenated derivatives the *cis* configuration only is present.

As to a possible free or hindered rotation of the halogenated alkyl group R around the R—CO bond, a comparison between found and calculated dipole moment values, and a qualitative consideration of internal steric and electrostatic factors, suggest that a single steric configuration is preferred in the monochloro and dichloro derivatives. The angle of 150° and 40° between the molecular plane containing the $COCHN_2$ grouping, and the plane defined by the C(carbonyl)—C(alkyl)—X (X = Cl in the former, H in the latter molecule) was found. A similar rigid structure is also expected in the parent molecule and, to a greater extent, in its trichloro derivative.

ALIPHATIC diazoketones are important intermediates in many organic reactions, and are involved in typical mechanisms of rearrangement.[1] The nature of the products depends on the steric conformation of these molecules, as far as the *cis–trans* equilibrium between the CO and CN_2 groups within the CO—CHN_2 moiety is concerned. As a substantial difference in the values of the dipole moment for the two configurations is expected, electric moment measurements should help to distinguish between them, and give an indication as to their relative importance. Free rotation of the two groups around the C—C bond is unlikely in the face of experimental data[2] which point to a rigid structure of the exatomic frame with all atoms in the same plane. This was also the premise of a recent theoretical paper[3] on the π-electron structure of some diazocompounds.

Dipole moments of some diazoalkanes and diazonaphthols have been recorded[4] but no such information is available for aliphatic diazoketones. Our results show that the CO—CHN_2 grouping is preferentially in the *cis* configuration under the experimental conditions used, and that there is a remarkable steric and electrostatic hindrance to free rotation of the halogenated alkyl group R (linked to the CO group) around the R—CO bond.

DISCUSSION

The present physico-chemical evidence suggests that diazoketones resonate between several canonical structures, the most significant being:

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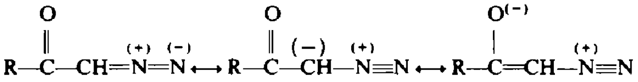

$$\underset{\text{I}}{R\text{—}\overset{\overset{\displaystyle O}{\|}}{C}\text{—}CH{=}\overset{(+)}{N}{=}\overset{(-)}{N}} \longleftrightarrow \underset{\text{II}}{R\text{—}\overset{\overset{\displaystyle O}{\|}}{C}\text{—}\overset{(-)}{C}H\text{—}\overset{(+)}{N}{\equiv}N} \longleftrightarrow \underset{\text{III}}{R\text{—}\overset{\overset{\displaystyle O^{(-)}}{|}}{C}{=}CH\text{—}\overset{(+)}{N}{\equiv}N}$$

This resonance requires coplanarity of all the atoms involved in the charge distribution; the relative contribution of forms II and III increases with the electron attracting power of the radical R. It follows, then, that the $COCHN_2$ grouping car assume two steric configurations in the molecular plane—*cis* (IV) or *trans* (V), as shown in Fig. 1, where the atomic orbitals useful for MO description of the bonds in these molecules are given. The structural data for diazomethane* suggest that the C atom of the CN_2 group is sp^2, and that the central and the terminal N atoms are sp hybridized. The latter can alternatively use its p atomic orbitals to form σ and π bonds. π_y Orbitals are bicentric and localized over the two N atoms which contribute one electron each for their formation. π_x Orbitals are strongly delocalized over al the atoms which possess suitable orbitals along the x direction; their behaviour depending on the number of these atoms, which in the present cases are five. Each atom contributes one electron, except the central N atom which gives two electrons to the delocalized π_x molecular orbitals.

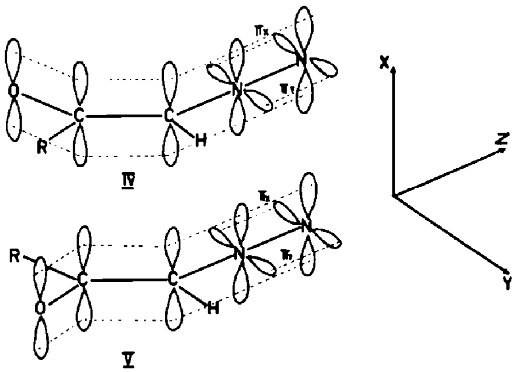

FIG. 1 *cis*-IV and *trans*-V configurations for aliphatic diazoketones.

The order of CN and NN bonds was evaluated using the above structural data for diazomethane and the Gordy's[5,]† approximate empirical relation. The figures obtained are: 1·70 for C—N and 2·77 for N—N, which compare favourably with those calculated[3] for the same molecule (1·65 and 2·73, resp). These authors gave the corresponding values for diazoacetone (1) as 1·54 and 2·81, and 1·50 for the C—C and 1·80 for the C—O bond order. This supports the additional contribution of structure III to the mesomeric system due to the enlarged conjugation within the $COCHN_2$ grouping.

The experimental dipole moments which, it is considered depend on the *cis–trans*

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* $r_{C—N}$ 1·32 Å; $r_{N—N}$ 1·12 Å; $H\widehat{C}N$ 116·5°; $H\widehat{C}H$ 127°.[2c]

† For the lengths of the "pure" single and double bonds the following values were taken: single C—N and N—N 1·47 Å, double C—N 1·27 Å, double N—N 1·25 Å.

conformation and on the possible hindered rotation at the C—C bond between the CO and the R radical C atoms, have been compared in Table 1 with those calculated for the structures most consistent with the experimental data and for different values of the angle ϑ between the plane of the conjugated chain (molecular plane) and that containing the C_2C_3X atoms (Fig. 2; X = Cl for the monochloro derivative (2) and H for the dichloro derivative (3). Calculated values for the *trans* form of the halodiazoketones have also been reported, although they appear to involve conformational situations incompatible with steric and electrostatic requirements (see below).

TABLE 1. OBSERVED AND CALCULATED DIPOLE MOMENTS (DEBYE UNITS)

Compound	ϑ	μ_{calc}^{trans}	ϑ	μ_{calc}^{cis}	μ_{obs}
CH_3COCHN_2		1·76		3·93	3·37
$CH_2ClCOCHN_2$	0°	3·54	0°	5·07	2·75[a]
	60^c	3·07	120°	3·37	
	75°	2·82	145°	2·85	
	90°	2·52	150°	2·79	2·80
			155°	2·71	
$CHCl_2COCHN_2$	0°	0·65[c] (0·32[b])	0°	2·23[c] (1·91[b])	
	45°	1·46[c] (1·24[b])	45°	2·68[c] (2·50[b])	2·65
	60°	1·60[c] —	60°	2·96[c] —	
CCl_3COCHN_2		—		2·69[d]	2·46

Parameters employed for the calculations:
$\widehat{NN}$ 1·12 Å;[e] CN 1·32 Å;[e] CH 1·08 Å;[e] CC 1·46 Å;[f] CO 1·21 Å;[f] C—CH_3 1·55 Å; C—Cl 1·76 Å;[f] $Cl\widehat{C}Cl$ 114 ± 4;[g] $H\widehat{C}N$ 116·5°;[e] $H\widehat{C}C$ 127°;[e] $O\widehat{C}C$ 125°; r(H) 1·2 Å; r(N) 1·5 Å; r(O) 1·40 Å; r(Cl) 1·80 Å; r(CH_3) 2 Å.

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[a] At 45°.

[b] Calculated by using a value 1·7 D for μ_{C-Cl} (Mansel Davies, *Some Electrical and Optical Aspects of Molecular Behaviour* p. 51. Pergamon Press (1965)).

[c] Calculated by using a value 1·34 D for μ_{C-Cl}, which accounts for a decrease of 0·36 D in the moment, due to the mutual interaction between two equal dipoles (C. P. Smyth, *Dielectric Behaviour and Structure* p. 238. McGraw-Hill (1955)).

[d] Calculated by using a value 1·57 D for μ_{CCl_3} and a value of 142° for the $\widehat{CCO}$ (J. R. Partington, *An Advanced Treatise on Physical Chemistry*, Vol 5; p. 522. Longmans, London (1954)).

[e] From diazomethane structural data.[2e]

[f] Acrylic aldehyde and crotonic aldehyde structural data.[7]

[g] Trichloroacetic aldehyde structural data.[9]

For the calculation of the moments a CN_2 group moment of 1 D was assumed. This was deduced from the value (1·42 D) for diazomethane[6] where it points from the C atom to the N atoms, consistent with a slightly higher contribution of a canonical structure like I above. As a matter of fact, due to the large charge separation in the two most important structures of this molecule (like I and II), the expected value for the moment in each should be about 6 to 7 D with a resultant of about 1 D. The introduction of carbonyl and halogenated groups as in the present diazoketones, lowers the diazogroup moment owing to the contribution of the canonical structure III. Although this precludes an easy evaluation of the CN_2 group moment, it was checked that a 10% variation of the CN_2 moment did not change appreciably the calculated moments. 1 D was taken as the difference between the total moment value (1·42 D) and the accepted resultant moment due to the two C—H bonds (0·4 D), which acts in the same direction as the main one. As reference models for the structural parameters adopted, acrylic and crotonic aldehydes were chosen[7] for the conjugated CO bond distance and the C_1C_2 bond distance (Fig. 2) between the α,β conjugated groups.

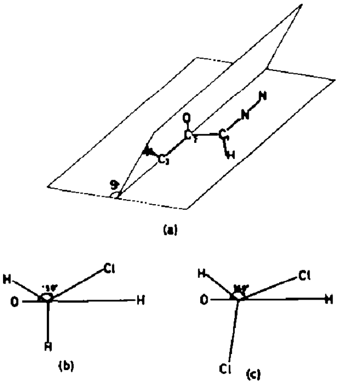

Fig. 2 Orientation of the alkyl group for monochloro (b) and dichlorodiazoacetone (c) with respect to the molecular plane, whose projection is represented by the O—H segment.

Following these premises, a comparison between the calculated (uncorrected for induced moments) and the observed moments indicates a preferred *cis* configuration (IV) for all of the examined compounds (see discussion on this point), except diazoacetone where the *trans* (V) is in equilibrium with the *cis* form (IV). By means of the equation $\mu^2_{obs} = x \cdot \mu^2_{cis} + (1 - x)\,\mu^2_{trans}$ where the observed μ_{obs} and the calculated μ_{cis} and μ_{trans} total moment values for the two forms were introduced, a [*cis*]/[*trans*] = 4·5 ratio for this molecule was found. From this figure a standard free energy for *trans*–>*cis* isomerization of +0·89 kcal/mole at 25° was evaluated. This figure compares favourably with the values reported[2f] +0·79 kcal/mole at −40° in deuterochloroform for the same molecule at 20% weight concentration, and +1·16 kcal/mole at 40% weight, as the effects due to the differences in medium and temperature (these authors claim that there is no appreciable concentration effect) should approximately balance each other.

The *cis* conformation is preferred owing to steric hindrance between the alkyl and diazo groups, operative in the *trans* form as shown by the Van der Waals radii (Table 1). Free rotation of the CH_3 group around the C_2—C_3 bond (Fig. 2a) may be possible but the electrostatic attraction between the strong C—O dipole and one of the three C—H dipoles may necessitate that an H is in the molecular plane facing the O atom. This would be a stronger requirement in the case of the *trans* conformation, because of the steric hindrance and of electrostatic repulsion between the C—H and C—N bond dipoles (see the charge distribution on the atoms[3] and the canonical structures above).

In monochlorodiazoacetone, a comparison between the experimental and calculated dipole moments definitely indicates that the *cis* form is the more stable, and that no Cl atom of the halogenated group lies on the molecular plane. Figure 2 shows the expected steric situation. The 150° angle (Table 3 and Fig. 2b) between the molecular plane and that defined by the $C_2—C_3—Cl$ atoms is the best compromise between steric and electrostatic effects. In fact, the electrostatic repulsion between the two large $\mu_{C—Cl}$ and $\mu_{C=O}$ bond dipoles and the attraction between $\mu_{C—Cl}$ and the methine group $\mu_{C'—H}$, coupled with the steric hindrance of the relative groups, resemble similar effects discussed[8] for $ClCH_2COCH_3$ and $ClCH_2COCl$ molecules, where a 150° figure was evaluated for an angle similarly defined.

A conformation very similar to that described above is found in dichlorodiazoacetone (Table 1 and Fig. 2c) in which an exchange of the H for the Cl atoms gives an approximate picture of the molecule. It differs from the previous one in that the Cl atom most remote from the O atom lies on a plane which makes an angle of about 160° with the molecular plane. This is at least 10° larger than the former; however, no easy meaning can be attached to this difference, because of the approximation made in our calculations; in particular, the true extent of the induced dipoles and of the distortion in the tetrahedral angles is uncertain.

The same limitations are involved in the calculated moment of the trichlorodiazoacetone, in which if 1·57 D for the CCl_3 group moment and 142° for the CCO angle were taken, the *cis* configuration would still be the preferred. Further, although the angle of rotation around the $C_2—C_3$ bond is uncertain, it is reasonable to use the structural parameters given in Table 3 to deduce that there is no free rotation of the CCl_3 group and that no Cl atom can eclipse the O atom.

In conclusion, it is clear that the CO and CN_2 groups are in *cis*-configuration in the three halogenated molecules examined, while an equilibrium exists between this and the *trans* configuration in the parent molecule. In fact, the calculated moments for the *trans* configuration in the three halogenated molecules either differ from the experimental ones, or are inconsistent with internal steric and electrostatic requirements. The last one is the situation for the monochlorodiazoacetone in which the calculated dipole moment value, 2·82 D, for the *trans* configuration is close to that found experimentally, yet the condition of minimum in the potential energy curve relative to the rotation of the CH_2Cl group around the $C_2—C_3$ bond is not satisfied. For this molecule the moment was also determined at 45° (Table 1) and found equal to that at 25° allowing for the limits of accuracy. More measurements are required for a stronger evidence, but it seems reasonable to think that a high activation energy is involved in the *cis–trans* isomerization in all of the halogen substituted molecules.

EXPERIMENTAL

Materials. Diazoacetone (**1**), ω-chlorodiazoacetone (**2**), ω-dichlorodiazoacetone (**3**) and ω-trichlorodiazoacetone (**4**) were prepared by reaction of excess diazomethane with the appropriate acid chloride.[10] Compounds **1**, **2** and **3** were purified by a threefold distillation under reduced press and **4** by repeated crystallization from anhyd ethyl ether at low temp. Benzene Carlo Erba RP was used throughout as solvent, without further purification.

Physical measurements. Dielectric measurements were made with a Dipolmeter WTW DM01 at 25 ± 0·1°, unless otherwise stated. The temp was kept constant at ±0·02° in order to have a reproducibility in the measured dipole moment value of 0·02 D.[11] The sensitivity in the dielectric constant measurements $\Delta\varepsilon/\varepsilon$, with the cell used, was 4×10^{-5} at 2 MHz frequency. As these molecules absorb in the visible

TABLE 2

CH_3COCHN_2 (1)			$CH_2ClCOCHN_2$ (2)			$CH_2ClCOCHN_2$ at 45°		
$W_2 . 10^3$[a]	ε_{12}[b]	V_{12}[c]	$W_2 . 10^3$	ε_{12}	V_{12}	$W_2 . 10^3$	ε_{12}	V_{12}
0·48	2·2796$_2$	1·1444$_1$	3·13	2·2940$_6$	1·1435$_1$	3·05	2·2536$_9$	1·1728$_1$
0·93	2·2855$_2$	1·1443$_8$	6·60	2·3185$_0$	1·1425$_1$	5·27	2·2684$_5$	1·1721$_3$
1·50	2·2940$_1$	—	9·33	2·3363$_6$	1·1411$_4$	7·12	2·2802$_9$	1·1706$_2$
1·82	2·2991$_4$	1·1442$_5$	13·27	—	1·1398$_4$	9·82	—	1·1696$_3$
2·58	2·3098$_2$	1·1442$_0$	15·44	2·3815$_0$	1·1389$_4$	11·38	2·3089$_4$	1·1690$_3$
3·13	2·3177$_1$	1·1441$_1$	19·20	2·4075$_0$	—	13·50	2·3228$_0$	1·1683$_7$

$CHCl_2COCHN_2$ (3)			CCl_3COCHN_2 (4)		
$W_2 . 10^3$	ε_{12}	V_{12}	$W_2 . 10^3$	ε_{12}	V_{12}
0·72	2·2769$_2$	1·1441$_4$	3·76	2·2895$_1$	1·1428
1·18	2·2797$_7$	1·1439$_1$	9·69	2·3140$_1$	1·1396
3·55	2·2914$_7$	1·1427$_8$	14·15	2·3347$_5$	1·1373
6·72	2·3067$_7$	1·1413$_0$	19·95	2·3528$_3$	1·1347
7·45	2·3108$_9$	—	32·30	2·3918$_3$	1·1276

[a] Solute weight fraction (g solute/g soln).

[b] Dielectric constant of the solution.

[c] Specific volume of the solution.

TABLE 3

Compound	ε_1[a]	α[b]	V_1[c] (cc)	β[d]	Pe (cc)	$Po + Pa$ (cc)	μ (D)
CH_3COCHN_2	2·2724	14·144	$1{\cdot}1444_9$	−0·150	20·7	233·3	3·37
$CH_2ClCOCHN_2$	2·2714	7·090	$1{\cdot}1446_2$	−0·365	25·5	160·1	2·80
	2·2333[e]	6·629	$1{\cdot}1745_4$	−0·430	25·5	154·7	2·75
$CHCl_2COCHN_2$	2·2726	4·975	$1{\cdot}1445_1$	−0·467	30·3	143·6	2·65
CCl_3COCHN_2	2·2797	3·555	1·1448	−0·528	35·2	124·3	2·46

[a] Dielectric constant of the solvent, obtained by extrapolating to infinite dilution the solution values.

[b] $\Delta\varepsilon_{12}/\Delta W_2$ (see Table 2).

[c] Specific volume of the solvent, obtained by extrapolating to infinite dilution the solution values.

[d] $\Delta V_{12}/\Delta W_2$ (see Table 2).

[e] Values for 45 ± 1°C.

region, the experimental determination of their molar refraction was prevented. It was, therefore, calculated using group and bond refraction values from literature.[12] The R_D value (7·9 cc) for the CN_2 group evaluated by Lindemann *et al.*[2a] for diazomethane, was applied without correction although a large optical exaltation of this group in the conjugated diazoketones was expected in view of the high value of the total molar polarization, as even a change of 20% in the value of R_D for CN_2 did not affect appreciably the value of the measured total moment. The atomic polarization throughout was considered negligible. The molar refraction so evaluated was considered equal to the molar distortion polarization. The following relations were employed for the density and the dielectric constant of benzene respectively; $d_t = d_{25} + 10{,}668 \times 10^{-5}(25\text{-}t)$ g/cc and $\varepsilon_t = \varepsilon_{15} - 0{\cdot}0019_8\,(t\text{-}15)$, where $d_{25} = 0{\cdot}8737_8$ g/cc at 25° and $\varepsilon_{15} = 2{\cdot}2925$ at 15°. The dielectric constant of air both at 25° and at 45° was taken to be 1·0006.[13] The total solute molar polarization at infinite dilution was calculated by the Halverstadt and Kumler method.[14] In the range of concentrations investigated, specific volume and dielectric constant plots for the solutions against the solute weight fraction were linear. The least square method was used in all calculations. As stated, the uncertainty in the value of the experimental quantities secured a reproducibility of 0·02 D in the value of the dipole moment.

All the experimental data are given in Table 2 while Table 3 presents the parameters used in the evaluation of the electric moments. IR frequencies for NN and CO stretching modes, obtained with a Perkin–Elmer 521 Spectrophotometer in CCl_4 and CS_2 solns under standard conditions, are as follows (cm^{-1} units): compound (**1**), ν(NN) 2103, ν(CO) 1663; (**2**), 2110, 1646; (**3**), 2110, 1660; (**4**), 2114, 1683.

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