Molecular Conformation of Diazo-compounds. Part IV.[1] Dipole Moments and Infrared Spectra of Some Hindered α-Diazo-ketones

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The conformations of the hindered diazo-ketones $MeCOCMeN_2$, $Bu^tCOCBu^tN_2$, $PhCOCMeN_2$, and *o*- and *p*-$ClC_6H_4COCMeN_2$ have been estimated in non-polar solvents from dipole moment and i.r. data. The t-butyl derivative has a single distorted configuration, with an angle of 140° between the planes containing the Bu^tCO and CBu^tN_2 systems. The results for the other compounds point to the occurrence of two pseudo-*cis–trans*-(distorted) conformers, with the possibility of partial diazo-group–carbonyl conjugation. In the *ortho*-chloro-derivative, where the phenyl ring is out of the $COCRN_2$ (pseudo) molecular plane, both conformers should be almost planar. In the light of evidence on the thermal decomposition of these compounds, it is inferred that complete planarity of the *cis–trans*-conformers is not a prerequisite for the formation of ketens or unsaturated ketones; rather, their formation is related to the angle of rotation around the central C–C bond.

In previous papers [1] the molecular conformation of some aliphatic and aromatic α-diazo-ketones has been reported. It was inferred for diazoacetone, $MeCOCHN_2$, at room temperature in a non-polar solvent that a *cis–trans*-equilibrium between planar conformers around the central C–C bond is operative. In *meta*- and *para*-substituted aromatic derivatives the steric hindrance due to the *ortho*-hydrogen atoms stabilizes the *cis*-form. Rotation of the ring out of the $COCHN_2$ molecular plane,† as in *o*-chlorodiazoacetophenone, releases this interaction and allows both conformers to occur.

In all these α-diazo-ketones the carbonyl stretching frequency is lower than in the corresponding ketones, while the N–N asymmetric stretching frequency is higher than in structurally related diazohydrocarbons. An explanation was proposed [2] in terms of a contribution from a triply-bonded polar mesomeric form $^{-}OCR{=}CH{-}\overset{+}{N}{\equiv}N$, with delocalized π electrons in the almost planar carbonyl-diazo-system.

The present work clarifies, by determining the molecular conformation of some strongly hindered α-diazo-ketones, whether such mesomeric forms are compatible with molecular structures increasingly distorted about the central C–C bond. In addition, we ascertain the relationship between the degree of molecular distortion and the ability of the α-diazo-ketone to undergo a Wolff rearrangement to give a keten.[3]

EXPERIMENTAL

Materials.—The compounds $MeCOCMeN_2$, $PhCOCMeN_2$, and *o*- and *p*-$ClC_6H_4COCMeN_2$ were prepared by treating dimethyldiazomethane with the corresponding acid chloride in anhydrous ethyl ether at −40 °C in the presence of trimethylamine.[4] They were purified by distillation under reduced pressure. The t-butyl derivative $Bu^tCOCBu^tN_2$ was obtained by oxidizing the corresponding monohydrazone with mercury trifluoroacetate,[5] and was purified by column chromatography. The purity of all the compounds was checked by mass spectrometry.

Physical Measurements.—These were performed at 25 °C in benzene (Erba RP grade) solution as previously [1a] described. The deformation polarization ($P_E + P_A$) was put equal to the molar refraction R_D and estimated from bond and group contributions.[6] The CN_2 group refraction was assumed to be 7·9 cm³.[7] The solute total polarization at infinite dilution was calculated by the Halverstadt–Kumler method.[8] I.r. spectra were obtained with a Perkin-Elmer model 521 i.r. spectrophotometer for CCl_4 solutions under standard conditions.

Calculation of Theoretical Dipole Moments.—For this purpose the following group moments were assumed: $\mu(\overset{\longleftarrow\!\!+}{C_{al}{-}CH_3})$ and $\mu(\overset{\longleftarrow\!\!+}{C_{al}{-}H})$ 0·4 D,[2a] $\mu(\overset{+\!\!\longrightarrow}{C{=}O})$ 2·7 D,[9a] and $\mu(\overset{+\!\!\longrightarrow}{C{-}Cl})$ 1·59 D.[9b] Owing to the variation in N–N asymmetrical stretching frequencies in the present molecules as compared with those previously examined, the following values were adopted for the diazo-group moment:‡ compound, ν(N–N), $\mu(C{-}N_2)$; $MeCOCMeN_2$, 2069 cm^{-1}, 1·15 D; $PhCOCMeN_2$, 2068 cm^{-1}, 1·15 D; *p*-$ClC_6H_4COCMeN_2$, 2068 cm^{-1}, 1·15 D; *o*-$ClC_6H_4COCMeN_2$, 2076 cm^{-1}, 1·10 D; $Bu^tCOCBu^tN_2$, 2057 cm^{-1}, 1·20 D.

The $\widehat{C{-}C{-}C}$ angle at the diazo-group was assumed to be that for diazomethane;[1a] the $\widehat{C{-}C{-}O}$ angle involving the central C–C bond was taken as 125°.[1a]

RESULTS AND DISCUSSION

Dipole Moments.—A comparison of the observed and calculated moments for the aliphatic compound $MeCOCMeN_2$ (μ_{cis} 3·9, μ_{trans} 1·7, $\mu_{obs.}$ 2·45 D) [1a] indicates that it cannot exist in a non-polar solvent as a single planar *cis*- or *trans*-conformer. Equilibrium between such conformers or free internal rotation round the central C–C bond are also ruled out owing to the par-

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† The $COCHN_2$ group is here assumed to be essentially planar.

‡ For a discussion of the relationship between $\mu(C{-}N_2)$ and ν(N–N) see ref. 1*c*.

[1] (*a*) Part I, G. Piazza, S. Sorriso, and A. Foffani, *Tetrahedron*, 1968, **24**, 4751; (*b*) Part II, S. Sorriso, G. Piazza, and A. Foffani, *J. Chem. Soc.* (*B*), 1971, 805; (*c*) Part III, S. Sorriso and A. Foffani, *J.C.S. Perkin II*, 1973, 1497.

[2] A. Foffani, C. Pecile, and A. Ghersetti, *Tetrahedron*, 1960, **11**, 285.

[3] F. Kaplan and G. K. Meloy, *J. Amer. Chem. Soc.*, 1966, **88**, 950.

[4] V. Franzen, *Chem. Ber.*, 1957, **602**, 199.

[5] M. S. Newmann and A. Arkell, *J. Org. Chem.*, 1959, **24**, 385.

[6] A. I. Vogel, *Chem. and Ind.*, 1950, 358.

[7] H. Lindemann, A. Wolter, and R. Groger, *Ber. deutschen chem. Gesellschaft*, 1930, **63**, 702.

[8] I. F. Halverstadt and W. D. Kumler, *J. Amer. Chem. Soc.*, 1942, **64**, 2988.

[9] (*a*) M. Davies, ' Some Electrical and Optical Aspects of Molecular Behaviour,' Pergamon, London, 1965; (*b*) R. J. W. Le Fèvre, ' Dipole Moments,' Methuen, London, 1964.

ticularly strong steric interaction between the methyl groups which takes place in the *cis*-configuration; *e.g.*, the methyl overlap in the planar *cis*-form of diacetyl, which is structurally very similar to methyldiazoacetone, is *ca.* 1·2 Å.[10a,*] The alternatives are therefore (*a*) an equilibrium between pseudo-*cis–trans*- (distorted) conformers, or (*b*) a single highly distorted structure (fixed or with restricted internal rotation) with a mean azimuthal angle of 120° between the planes containing the MeCO and $MeCN_2$ functions.

TABLE 1

Experimental results

$MeCOCMeN_2$

10^3w_2	ε_{12}	$V_{12}/cm^3\ g^{-1}$
1·20	2·2804	1·1444
2·35	2·2874	1·1444
4·71	2·3020	1·1445
6·00	2·3090	1·1445
7·50	2·3191	1·1446
9·00	2·3283	1·1446

$Bu^tCOCBu^tN_2$

10^3w_2	ε_{12}	$V_{12}/cm^3\ g^{-1}$
1·05	2·2742	1·1444
2·20	2·2766	1·1443
3·38	2·2790	1·1443
4·92	2·2822	1·1442
6·85	2·2863	1·1442
8·30	2·2893	1·1441

$PhCOCMeN_2$

10^3w_2	ε_{12}	$V_{12}/cm^3\ g^{-1}$
1·55	2·2798	1·1440
2·09	2·2826	1·1438
3·71	2·2908	1·1435
4·63	2·2955	1·1433
5·89	2·3019	1·1430
7·40	2·3095	1·1426

p-$ClC_6H_4COCMeN_2$

10^3w_2	ε_{12}	$V_{12}/cm^3\ g^{-1}$
1·25	2·2773	1·1440
2·43	2·2817	1·1436
3·67	2·2862	1·1433
4·90	2·2907	1·1429
6·27	2·2958	1·1425
8·15	2·3027	1·1420

o-$ClC_6H_4COCMeN_2$

10^3w_2	ε_{12}	$V_{12}/cm^3\ g^{-1}$
1·38	2·2801	1·1440
2·30	2·2913	1·1433
3·15	2·2962	1·1430
6·37	2·3092	1·1421
8·50	2·3215	1·1413

TABLE 2

Parameters used in calculating observed dipole moments

Compound	ε_1	α	$V_1/cm^3\ g^{-1}$	β	R_D/cm^3	$P_{2\infty}/cm^3$	μ/D
$MeCOCMeN_2$	2·2730	6·150	1·1444	0·022	25·3	147·5	2·45
$Bu^tCOCBu^tN_2$	2·2720	2·082	1·1445	−0·031	53·2	133·6	1·98
$PhCOCMeN_2$	2·2720	5·081	1·1443	−0·230	45·1	196·7	2·75
p-$ClC_6H_4COCMeN_2$	2·2728	3·669	1·1443	−0·288	49·8	135·9	2·05
o-$ClC_6H_4COCMeN_2$	2·2721	5·800	1·1445	−0·381	49·8	256·6	3·18

The data for the t-butyl derivative, compared with those[11] for 2,2,5,5-tetramethylhexa-3,4-dione, $Bu^tCOCOBu^t$, point to a single highly distorted structure † with an azimuthal angle of *ca.* 140°, to be compared with a value of *ca.* 130° for the corresponding diketone. The difference should mainly depend on the CCN_2 angle being greater than that of CCO,‡ and on the uncertainty in the choice of the group moments.

The aromatic compounds $PhCOCMeN_2$ and *p*-$ClC_6H_4COCMeN_2$ cannot have planar conformations (for $PhCOCMeN_2$ μ_{cis} 3·7, μ_{trans} 1·5, μ_{obs} 2·75 D; for *p*-$ClC_6H_4COCMeN_2$ μ_{cis} 3·0, μ_{trans} 1·9, μ_{obs} 2·05 D).[1b] The alternatives are therefore (*a*) two pseudo-*cis–trans*-conformers in equilibrium, slightly distorted about both the diazo–carbonyl and phenyl–carbonyl C–C bonds or (*b*) a single highly distorted structure, whose azimuthal angle is *ca.* 110 and 130° in the parent molecule and in the *para*-derivative, respectively.

For the *ortho*-derivative, assuming, on the basis of results[1c] for *o*-chloroacetophenone and *o*-chlorodiazoacetophenone, that the chlorine–oxygen steric interaction forces the phenyl ring out of the molecular plane by *ca.* 105°, the observed moment is compatible with a planar *cis–trans*-conformation (μ_{cis} 4·2, μ_{trans} 2·0, $\mu_{obs.}$ 3·18 D). Distortion about the diazo–carbonyl C–C bond, even if present, should be smaller than in the other aromatic compounds. The *cis* : *trans*-ratio is 42 : 58.

I.r. Spectra.—The i.r. information, compared in Table 3 with results from ref. 1, is in general agreement with the deductions above and allows some additional indication of the electronic and steric situation. (*a*) The characteristic feature of the aromatic α-diazo-ketones with an alkyl or aryl substituent in the diazo-group [compounds (5), (7), (8), and (10) in Table 3] is the drastic lowering of the N–N asymmetric stretching frequency to the mean range for diazohydrocarbons (see, *e.g.* the value for dimethyldiazomethane), while the CO stretching frequency is only slightly affected. Taking into account the possible conformations suggested by the dipole moment data, this indicates that the substituent exerts an electronic influence (inductive and/or mesomeric) on the diazo-group, favouring structures with double-bond character at the N–N linkage, typical of diazohydrocarbons (see ref. 1*c*). A steric effect due to

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* The information for diacetyl shows some discrepancies. Electron diffraction data[10b] suggesting a planar *trans*-conformation do not exclude the presence of a small amount of the *cis*-form. A study of the temperature dependence of the dipole moment[10c] leaves unsettled the alternative of a *cis–trans*-equilibrium or a prevalence of the *trans*-form in a planar configuration. Solid state information[10d] and the study of emission spectra[10e] point to the presence of the *trans*-form only. On the contrary, the negative value of the molar Kerr constant in solution[10a] and the low dipole moment (1·08 D) favour the presence of a single somewhat distorted structure.

† Dipole moment data for $Bu^tCOCOBu^t$ for a limited range of temperature[11] did not give any evidence on possible restricted internal rotation; u.v. absorption spectra[12] indicate an azimuthal angle between 110 and 150°.

‡ The n.m.r. spectrum[3] of the mono t-butyl derivative Bu^tCOCHN_2 shows indeed that the *cis*-conformer is highly preferred, apparently due to the steric interaction of the t-butyl and diazo groups in the *trans*-conformation.

[10] (*a*) P. H. Cureton, C. G. Le Fèvre, and R. J. W. Le Fèvre, *J. Chem. Soc.*, 1961, 4447; (*b*) J. E. Lu Valle and V. Schomaker, *J. Amer. Chem. Soc.*, 1939, **61**, 3520; (*c*) G. I. M. Bloom and L. E. Sutton, *J. Chem. Soc.*, 1941, 727; (*d*) S. Mizushima, ' Structure of Molecules and Internal Rotation,' Academic Press, New York, 1954, p. 75; (*e*) J. W. Sidman and D. S. McClure, *J. Amer. Chem. Soc.*, 1955, **77**, 6461.

[11] S. Sorriso and S. Santini, unpublished results.

[12] N. J. Leonard and P. M. Mader, *J. Amer. Chem. Soc.*, 1950, **72**, 5388.

this substitution could also be important, in that it should increase the $C-\hat{C}-C$ angle at the diazo-group and so modify the hybridization at the diazo-group itself. (*b*) The fact that the CO stretching frequency is almost invariant, remaining in the range characteristic of aromatic diazoketones, suggest that the preferred conformation for these molecules should be that involving two slightly distorted *cis*–*trans*-conformers. Such a distortion, which contributes to the lowering of the N–N stretching frequency, should still allow some carbonyl–diazo conjugation.* The reduced degree of conjugation is apparently counterbalanced by the aryl–carbonyl electronic interaction and by the increased steric effect on the carbonyl carbon, both factors lowering the CO stretching frequency (see ref. 1*b*). (*c*) The importance of steric effects is particularly evident by the results for *ortho*-derivatives and for hindered aliphatic compounds [compounds (2), (3), (8), and (9)]. In fact, as the aryl ring in the *ortho*-derivatives is forced out of the carbonyl–diazo pseudo-molecular plane (see ref. 1*c* and above), the chlorine atom should act solely inductively and possibly by a dipolar field effect [14] on the carbonyl group, so that the steric influence of the methyl group on the hybridization of the carbonyl carbon atom should determine the lowering of the CO force constant. In the case of the aliphatic compounds, the situation for the t-butyl derivative, in which owing to the highly distorted structure suggested by the dipole moment data almost no carbonyl–diazo-electronic interaction should operate, is remarkable in that the combined action of the inductive and steric effects of the t-butyl groups causes the carbonyl frequency to fall, in an apparently fortuitous manner, to the same range as the aromatic derivatives.

TABLE 3

I.r. stretching frequencies

Compound	ν(C=O)/cm^{-1}	ν(N–N)/cm^{-1}
$MeCOCHN_2$ (1)	1659	2107
$MeCOCMeN_2$ (2)	1648 [a]	2069 [a]
$Bu^tCOCBu^tN_2$ (3)	1633 [a]	2057 [a]
$PhCOCHN_2$ (4)	1634	2108
$PhCOCMeN_2$ (5)	1629 [a]	2068 [a]
p-$ClC_6H_4COCHN_2$ (6)	1632	2109
p-$ClC_6H_4COCMeN_2$ (7)	1627 [a]	2068 [a]
o-$ClC_6H_4COCHN_2$ (8)	1624 [b]	2104 [b]
o-$ClC_6H_4COCMeN_2$ (9)	1630 [a]	2076 [a]
$PhCOCPhN_2$ (10)	1636	2072
CH_2N_2 (11)		2088 [c]
Me_2CN_2 (12)		2074 [a,c]

[a] Present work. [b] Ref. 1*c*; all other values from ref. 2. [c] Taken for ether solution.

Wolff Rearrangement and Molecular Conformation.—It was suggested,[3] from n.m.r. measurements and from experimental evidence [15] on the reactivity of α-diazoketones, that the reaction path to give a keten requires a planar *cis*-conformation for the diazo-compound. The present results, which point to distorted structures for hindered diazo-ketones which give measurable amounts of keten, allow this suggestion to be improved. A concerted mechanism involving migration of an alkyl or aryl group and detachment of nitrogen is compatible with a slightly distorted pseudo-*cis*-conformer and even with a single distorted structure. The angle of rotation of the central C–C bond is the determining factor in this regard.†

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* In diphenyl sulphide, where the phenyl groups are forced by *ca.* 40° [13] out of the plane containing the C–S–C group, it has been suggested that the C–S bonds still retain *ca.* 20% double-bond character.

† It is remarkable that, both for $Bu^tCOCBu^tN_2$ [5] and $PhCOCMeN_2$,[4] the formation of unsaturated ketone observed experimentally (80—92 and 72% respectively) corresponds closely to the molecular distortion between the (real or hypothetical) planar conformers.

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[14] L. J. Bellamy and R. L. Williams, *J. Chem. Soc.*, 1956, 3704; 1957, 4294; R. N. Jones, W. F. Forber, and W. A. Mueller, *Canad. J. Chem.*, 1957, **35**, 504.

[15] F. Arndt and R. Eistert, *Ber.*, 1935, **68**, 200; G. Grundmann, *Annalen*, 1936, **524**, 31; 1938, **536**, 29; P. C. Guha and M. S. Muthanna, *Current Sci.*, 1938, **6**, 449.