Dipole Moments and Molecular Conformation of Diazo-compounds. Part III.[1] Benzoylphenyldiazomethane and Related Molecules

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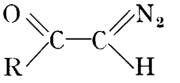
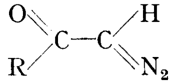
Dipole moment and i.r. data on benzoylphenyldiazomethane may be interpreted either through the occurrence, in non-polar solvents, of *cis–trans* rotational isomerism at the diazo-carbonyl linkage, with the diazo-carbonyl group virtually planar, or through a single distorted structure with an azimuthal angle of *ca.* 85° between the planes containing the Bz and $CPhN_2$ groups. For *o*-chlorodiazoacetophenone both *cis*- and *trans*-diazo-carbonyl conformers occur: the presence of a *trans*-diazo-carbonyl conformer, as distinct from the cases of the *meta*- and *para*-derivatives, is attributed to phenyl rotation out of the diazo–carbonyl molecular plane, which releases the steric hindrance of the *ortho*-hydrogen atom. The presence of a single distorted arrangement of the chlorine and carbonyl groups is suggested. For *m*-chlorodiazoacetophenone only the diazo-carbonyl *cis*-conformer is present: the chlorine atom and the carbonyl group may be both *cis* and *trans*.

ALIPHATIC and aromatic diazo-ketones were the subject of two previous papers.[1] For diazoacetone it was shown [1a] that, with the diazo-carbonyl group ($COCHN_2$) virtually planar, two conformational isomers are present.



cis



trans

In contrast, for diazoacetophenone and its *para*-substituted derivatives the *cis*-form predominates.[1b] This difference stems mainly from the greater steric hindrance due to the R group in the *trans*-form. This paper (a) provides information on possible competition between internal rotation around the phenyl–carbonyl and carbonyl–diazo bonds by examining the substitution of the methine hydrogen atom of diazoacetophenone by a phenyl group † and (b) reports on whether the reduction of steric hindrance between the phenyl and diazo-groups through rotation of the benzene ring itself suffices for the occurrence of a *trans*-form even for aromatic diazo-ketones.[1b]

TABLE 1

Experimental quantities and dipole moments for compounds (1)—(9)

Compound	ε_1	α	V/cm³ g⁻¹	β	$R_{\mathrm{D\ calc.}}$/cm³	P_a/cm³	$P_{2\infty}$/cm³	μ/D [a]	μ/D [b]	Lit. μ/D
Ph_2CN_2 (1)	2·2730	2·76	0·6118	0·25	62·0	3·8	103·7	1·30	1·37	1·42 [c]
(p-$MeC_6H_4)_2CN_2$ (2)	2·2735	3·86	0·6128	0·30	71·5	5·0	146·6	1·77	1·91	1·94 [c]
(p-$ClC_6H_4)_2CN_2$ (3)	2·2728	0·85	0·6132	0·12	71·3	6·6	79·9	0·30	0·65	0·65 [c]
$BzCPhNNH_2$ (4)	2·2730	6·24	1·1443	−0·22	68·0		324·9		3·54	
$BzCPhN_2$ (5)	2·2725	3·98	1·1445	−0·29	66·6		223·1		2·77	2·79 [d]
m-ClC_6H_4Ac (6)	2·2724	5·35	1·1445	−0·32	40·8		193·8		2·73	
m-$ClC_6H_4COCHN_2$ (7)	2·2725	6·77	1·1440	−0·32	44·6		272·9		3·34	
o-ClC_6H_4Ac (8)	2·2720	7·33	1·1443	−0·29	40·8		252·3		3·21	
o-$ClC_6H_4COCHN_2$ (9)	2·2730	7·38	1·1445	−0·12	44·6		304·7		3·56	

[a] $P_a \neq 0$. [b] $P_a = 0$. [c] Solvent carbon tetrachloride; $t = 0$ °C; $P_a = 0$; $P_{2\infty}$ is calculated from a $P_2 = P_2(f_2)$ plot (from N. V. Sidgwick, L. E. Sutton, and W. Thomas *J. Chem. Soc.*, 1933, 406). [d] Solvent benzene; $t = 25$ °C; $P_a = 0$ (from J. D. Anderson, R. J. W. Le Fèvre, and I. R. Wilson, *J. Chem. Soc.*, 1949, 2082).

EXPERIMENTAL

Materials.—The preparation of the diazo-compounds (1)—(3) (Table 1) has been described.[3] The hydrazone (4) (purum Fluka) was twice recrystallized from anhydrous ethanol, m.p. 147—148 °C. Benzoylphenyldiazomethane (5) was prepared by oxidation of the hydrazone (4) with mercuric oxide; [4] its m.p. [64—65 °C (decomp.), the same in two different preparations] was lower than the literature value [79 °C (decomp.)] but its analysis was correct (Found: C, 75·45; H, 4·45; N, 12·35. Calc. for $C_{14}H_{10}N_2O$: C, 75·65; H, 4·55; N, 12·65%). The diazo-ketones (7) and (9) were prepared [5] by treating excess of diazomethane with the appropriate acid chloride in anhydrous ether and were purified by three-fold crystallization at low temperature from the same solvent. The acetophenones (6) and (8), examined for comparison with the corresponding diazo-ketones, were Schuchardt products for analysis and were used without further purification. Carbon tetrachloride and benzene (RP Erba) were used throughout as solvents, the first for compounds (1)—(3) at 0 °C, the second for compounds (4)—(9) at 25 °C.

Physical Measurements.—Dielectric constants were measured as before,[1a] with special devices to keep the temperature of the dielectric cell at 0 °C. The densities were measured automatically (DMA 02 of Anton Paar K.G.), the uncertainty in the specific volume being estimated as ∓0·00007 cm³ g⁻¹. The total solute molar polarization at infinite dilution was calculated by the method of Halverstadt and Kumler.[6] The deformation polarization ($P_e + P_a$)

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† For recent theoretical calculations on the nature of rotational isomerism in diazoacetone and diazoacetophenone see ref. 2.

[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.

[2] I. G. Csizmadia, S. A. Houlden, O. Meresz, and P. Yates, *Tetrahedron*, 1969, **25**, 2121.

[3] N. V. Sidgwick, L. E. Sutton, and W. Thomas, *J. Chem. Soc.*, 1933, 406.

[4] C. D. Nenitzescu and E. Solomonica, *Org. Synth.*, 1951, **2**, 496.

[5] F. Arndt and J. Amende, *Ber.*, 1928, **61**, 1122.

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

was put equal to the molar refraction and was calculated using group and bond refraction values from the literature.[7] The atomic polarization was considered to be negligible for compounds (4)—(9); the dipole moments of the weakly polar compounds (1)—(3) were also estimated by assuming $P_a = 1{\cdot}9$, $2{\cdot}5$, and $3{\cdot}3$ cm^3 for benzene, toluene, and chlorobenzene, respectively.[8] The R_D value (7·9 cm^3) taken for the CN_2 group was that of Lindemann *et al.*[9] for diazomethane. In fact, because of the high total molar polarization even a 20% change in the R_D value for the CN_2 group did not appreciably affect the observed dipole moment. The uncertainty in the values of the experimental quantities (Table 1) allowed a reproducibility of ±0·02 D in the observed dipole moments, with the exception of compound (3) which had the lowest moment. I.r. stretching frequencies for the N–N and C=O bonds were obtained with a Perkin-Elmer model 521 spectrophotometer for carbon tetrachloride solutions under standard conditions.

RESULTS AND DISCUSSION

(a) *Diazo-compounds.*—Two resonance forms (I) and (II) make the main contribution to the structure of the diazo-group. Both forms influence the $\mu(CN_2)$ moment,

$$\underset{\text{(I)}}{R_2C{=}\overset{+}{N}{=}\overset{-}{N}} \longleftrightarrow \underset{\text{(II)}}{R_2\overset{-}{C}{-}\overset{+}{N}{\equiv}N}$$

which therefore is related to the ν(N–N) stretching vibration. Because of the shift to low frequency of this mode in benzoylphenyldiazomethane compared with other diazoketones[1] (2072, 2107, and 2108 cm^{-1} for $BzCPhN_2$, $AcCHN_2$, and $BzCHN_2$, respectively[10]), the value of the diazo-group moment to be used for this molecule was reconsidered. $\mu(C_{ar}{-}H)$ Being nearly zero,* the moment observed for diphenyldiazomethane (1·3 D) should be essentially that of the diazo-group.† The fact that the present value (1·3 D) is higher than that previously accepted (1·0 D)[1] is due to variations in the relative contribution of forms (I) and (II). The remarkably low ν(N–N) frequency observed for diazohydrocarbons with an aromatic ring directly linked to the diazo-group, points to an increased contribution of the double-bond form (I) and to an increased group moment. On the basis of the above arguments a value of 1·15 D for $\mu(\overset{+\!\longrightarrow}{CN_2})$ was assumed for benzoylphenyldiazomethane.

The dipole moment for $BzCPhN_2$ is compatible with two different molecular situations: (i) both *cis*- and *trans*-conformers are present; (ii) a single distorted conformer occurs.

(i) *Two conformers.* This alternative allows virtual planarity and efficient conjugation of the carbonyl and diazo-groups. The occurrence of this conjugation is shown by a comparison of the C=O and N–N stretching frequencies: ν(C=O) 1636, 1634, 1659, and 1691 cm^{-1} for $BzCPhN_2$, $BzCHN_2$, $AcCHN_2$, and BzMe, respectively; ν(N–N) 2042, 2062, 2072, and 2108 cm^{-1} for CPh_2N_2, $CHPhN_2$, $BzCPhN_2$, and $BzCHN_2$, respectively.[10] The *cis*-conformer is strongly hindered owing to the almost complete overlap of the van der Waals radii of the two adjoining hydrogen atoms *ortho* to the phenyl rings (Figure 1). The rings themselves, or at least one of them, must therefore rotate out of the molecular plane, as suggested for diazoacetophenone.[2,‡] On the other hand, there is evidence that a benzene ring directly bonded to a diazo-group influences it even when the two groups are not planar, *e.g.*, ν(N–N) for Ph_2CN_2 is much lower than for CH_2N_2 (2042 against 2088 cm^{-1}).[10] The minimum angle of rotation of each phenyl ring is *ca.* 28°, according to a van der Waals scale molecular model. As a result the *trans*-conformer, virtually absent in *para*-substituted diazoacetophenones,[1b] is as probable in benzoylphenyldiazomethane as the *cis*-one; this is apparently caused by a significant energy increase of the *cis*-form upon substitution of the methine hydrogen atom. On this basis, using the equation $\mu^2_{obs} = X \,.\, \mu^2_{cis} + (1 - X) \,.\, \mu^2_{trans}$ the *cis* : *trans* ratio was found to be 52 : 48. Both conformers should be somewhat distorted from planarity by

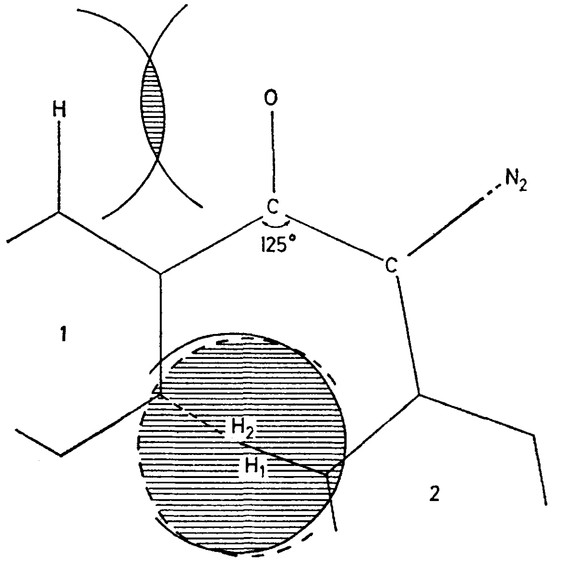

FIGURE 1 Molecular diagram of benzoylphenyldiazomethane (*cis*-diazo–CO)

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* This assumption, which has been adopted in situations structurally related to the present ones,[1b,11] is here used to make an internal comparison.

† Taking H–$\widehat{C}$–N 116° 30′ and H–$\widehat{C}$–H 127° as found for diazomethane,[12] and $\mu(\overset{+\!\rightarrow}{C{-}Cl}) = 1{\cdot}55$ and $\mu(\overset{\leftarrow\!+}{C{-}Me}) = 0{\cdot}4$ D[13] from the moments observed for ditolyl- and bis-(*p*-chlorophenyl)-diazomethane, values of 1·4 and 1·1 D respectively were obtained for the moment of the diazo-group.

‡ Csizmadia *et al.*[2] took for their calculation a mean value of 129° for the angle C–$\widehat{CO}$–C (our value 125°)[1b] for the *cis*-conformer of diazoacetophenone, with the phenyl ring 32° out of the molecular plane.

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

[8] J. R. Partington, 'An Advanced Treatise on Physical Chemistry,' Longmans, London, 1954, vol. 5, p. 381.

[9] H. Lindemann, A. Wolter, and R. Groger, *Ber.*, 1930, **63**, 702.

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

[11] O. Exner, Z. Fidlerova, and V. Jehlicka, *Coll. Czech. Chem. Comm.*, 1968, **33**, 2019.

[12] A. P. Cox, L. F. Thomas, and J. Sheridan, *Nature*, 1958, **181**, 1000.

[13] M. Davies, 'Some Electrical and Optical Aspects of Molecular Behaviour,' Pergamon, London, 1965.

internal rotation around their phenyl–carbonyl and carbonyl–diazo bonds, the first deviation being much greater than the second.

(ii) *A single distorted structure.* For this case, the planes of the carbonyl and diazo-groups should be rotated about one another by *ca.* 85°.* This conformational situation, which might also justify the observed moment, seems less plausible because it would not allow carbonyl–diazo conjugation and would not explain the i.r. behaviour of the carbonyl band. It may be noted that, for the 1,2-diketone benzil the observed moment [14] corresponds to a relative rotation of the carbonyl planes of *ca.* 75°; this molecule is, however, in a different electronic situation as shown by the much higher value of the carbonyl stretching frequency.

TABLE 2

Calculated dipole moments and stretching frequencies

Compound	μ_{cis}/D (Cl–CO isom.)	μ_{trans}/D (Cl–CO isom.)	μ_{obs}/D	ν(N–N)/cm^{-1}	ν(C=O)/cm^{-1}
m-Chloroacetophenone	4·07	1·60	2·73		1692
m-Chlorodiazoacetophenone (*cis*-diazo–CO)	4·54	2·14	3·34	2104	1630
o-Chloroacetophenone	4·44	2·26	3·21		1691
o-Chlorodiazoacetophenone (*cis*-diazo–CO)	5·28	3·48			
o-Chlorodiazoacetophenone (*trans*-diazo–CO)	3·10	0·90	3·56	2104	1624

In order to distinguish between the above alternatives, a dipole moment and spectral study is under way on the highly hindered compound $Bu^tCOCBu^tN_2$ and on related molecules, where diazo–carbonyl conjugation is almost ruled out.[15]

(b) ortho-*Chloro-derivatives.*—The moment observed for *o*-chloroacetophenone, intermediate between those calculated for the *cis*- and *trans*-planar conformers, referred to the relative position of the chlorine and oxygen atoms (see Table 2), can also be explained in two different ways. The first, an equilibrium between the two possible conformers, may be ruled out in view of the strong steric interaction between the chlorine and oxygen atoms in the *cis*-form (see Figure 2). This is supported by the shape of the carbonyl stretching band, which is much broader than for the *meta*- and *para*-derivatives but a singlet. With the scale dimensions of Figure 2, the minimum dihedral angle between the phenyl plane and that of the C(CO)C atoms cannot be less than 85°. A similar weaker interaction should be effective in the *trans*-form. The preferred structure probably has the phenyl ring out of the C(CO)C plane by an angle of *ca.* 105°. This angle, associated with which there may be restricted internal rotation, allows the reproduction of the experimental moment.

For *o*-chlorodiazoacetophenone, the extent of chlorine–oxygen interaction should not change significantly. It may be assumed that in this instance also the phenyl ring is forced out of the diazo–carbonyl molecular plane by a dihedral angle of about the same amount as suggested above. The carbonyl stretching band is enlarged but not split in this compound also. If the theoretical moments for the *cis*- and *trans*-conformers, referred to the relative position of the carbonyl and diazo-groups, are estimated, with the above assumption as to the steric situation of the phenyl ring, both forms are found to be present for *o*-chlorodiazoacetophenone, as distinct from the case for *para*-substituted derivatives and the parent molecule.[14] This result agrees with previous conclusion that the drastic shift of the *cis–trans* equilibrium towards the *cis*-form was due to large steric hindrance in the *trans*-form. In *o*-chloroacetophenone phenyl rotation releases this hindrance and allows both conformers to occur, as for diazoacetone.[1a] The *cis* : *trans* ratio is estimated to be 62 : 38.

(c) meta-*Chloro-derivatives.*—In view of the mesomeric effect (—*M*) of the carbonyl group it may be assumed, as for the *para*-derivatives, that in *m*-chloroacetophenone the phenyl ring is almost planar with the C(CO)C group because only a weak interaction of the chlorine atom with the carbonyl or methyl group is to be expected. The observed moment agrees (see Table 2) with the

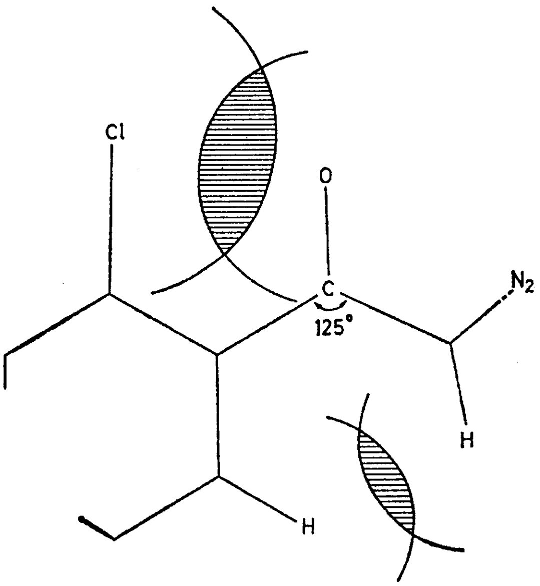

FIGURE 2 Molecular diagram of *o*-chlorodiazoacetophenone (*cis*-diazo–CO; *cis*-Cl–CO)

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* The following dipole moments (μ/D) were calculated at different angles: 0° (*cis*), 3·54; 30°, 3·44; 60°, 3·16; 80°, 2·88; 90°, 2·72; 180° (*trans*), 1·50.

[14] C. L. Caldwell and R. J. W. Le Fèvre, *J. Chem. Soc.*, 1939, 1614; P. H. Cureton, C. G. Le Fèvre, and R. J. W. Le Fèvre, *ibid.*, 1961, 4447.

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

presence of *cis*- and *trans*-conformers, again referred to the relative position of the chlorine and oxygen atoms, in the ratio *ca.* **38** : **62**. The ratio of the two conformers * is probably related to a slightly different energy of interaction between the chlorine atom and the carbonyl (or methyl) group.

In *m*-chlorodiazoacetophenone the van der Waals radii and the diazo and carbonyl stretching frequencies [ν(N–N) and ν(C=O) **2108** and **1630** cm^{-1}, respectively, against **2109** and **1633** cm^{-1} in *p*-chlorodiazoacetophenone] point to a structure having the $COCHN_2$ group almost planar and efficiently conjugated with the benzene ring. Therefore, considering the previous results,[1b] only the *cis*-conformer should be expected with reference to the carbonyl–diazo relative position. As with the corresponding ketone, the observed moment is consistent with the presence of *cis*- and *trans*-conformers, referred to the relative position of the chlorine and oxygen atoms. The ratio, **43** : **57**, is significantly close to that found for *m*-chloroacetophenone.

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* The ratio of these two conformers is hardly affected by the value of the $C-\widehat{CO}-C$ angle and by the carbonyl bond moment, here assumed, respectively, 125° [1b] and 2·7 D.[13]