Preferred Molecular Conformations of Benzoyl(diazo)phenylmethane and 1-Benzoyl-1-diazoethane by Semiempirical Molecular Orbital Calculations

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Semiempirical CNDO/2 calculations have been carried out for benzoyl(diazo)phenylmethane and 1-benzoyl-1-diazoethane. From the energy values obtained it is concluded that two rotamers, in slow interconversion, exist for benzoyl(diazo)phenylmethane and that similar rotamers, but in rapid interconversion, exist for the 1-benzoyl-1-diazoethane. The predicted effects of these interconversions on the electric dipole moments and i.r. spectra are in good agreement with the experimental data.

In previous papers, studies of the rotational isomerism of the molecules $PhCOCHN_2$ and $MeCOCHN_2$ using Hofmann's extended Hückel method [1] and of $CH_2ClCOCHN_2$ and $MeCOC(Me)N_2$ using the CNDO/2 semiempirical MO method [2] have been reported. For all four molecules, the results of these calculations were in good agreement with experimental results from n.m.r.[3]

[1] I. G. Csizmadia, S. A. Houlden, O. Meresz, and P. Yates, *Tetrahedron*, 1969, **25**, 2121.
[2] S. Sorriso, F. Stefani, A. Flamini, and E. Semprini, *J.C.S. Faraday II*, 1975, 682.
[3] F. Kaplan and G. K. Meloy, *J. Amer. Chem. Soc.*, 1966, **88**, 950.

and i.r.[4,5] spectra and electric dipole moments.[6-8] This has encouraged us to extend the study, using the CNDO/2 method, to the compounds $PhCOC(Ph)N_2$ and $PhCOC(Me)N_2$ previously examined by means of other techniques [4,5,8,9] and for which the conformational results need to be completed.

For benzoyl(diazo)phenylmethane the electric dipole moment [9] is compatible with either of two more or less distorted *cis–trans*-conformers in equilibrium and also with only a single conformer of the skew type. Splitting of the asymmetric N–N stretching vibration has been interpreted as due to the presence of two forms.[4,5] The same is the case for the 1-benzoyl-1-diazoethane, the dipole moment [8] not providing sufficient evidence to distinguish between two possibilities analogous to those in the corresponding phenyl derivative. However, for the diazoethane derivative the asymmetric N–N stretching mode gives only a single absorption and this was interpreted as due to the presence of only one configuration.[4] This is not sufficient evidence, however, to prove the existence of only one conformer since if there is rapid interconversion between two forms, i.r. techniques cannot distinguish between them.

The present theoretical calculations aim at obtaining information not only on the conformation but also on the electronic and steric effects present in these molecules. Further knowledge of the role of these effects would allow us to clarify the mechanism of the *cis* $\rightleftarrows$ *trans*-interconversion in benzoyl(diazo)phenylmethane and of internal rotation in 1-benzoyl-1-diazoethane.

RESULTS AND DISCUSSION

As mentioned above, the molecules investigated theoretically in previous work were $PhCOCHN_2$, $MeCOCHN_2$,[1] $CH_2ClCOCHN_2$, and $MeCOC(Me)N_2$.[2] Since the results obtained were in good agreement with experiment,[3-8] the calculations for the present molecules were carried out using the same angles and distances. The semiempirical CNDO/2 method of Pople [10] was used for the calculations, which were performed on a UNIVAC 1110 computer at the University of Bergen, using a program supplied by the QCPE organization.[11] No modifications of parameters were introduced. The transformation from bond distances and angles were performed by a special program COORD.[12]

(a) *Benzoyl(diazo)phenylmethane*.—The geometrical parameters used for this molecule are those shown in Figure 1 and were kept constant for all the calculations. These were carried out for α values between 0 and 90° with a periodicity of 30°. For each angle α the angle γ was allowed to vary between 0 and 90° at 30° intervals. Finally, for each pair of (α, γ) angles, the angle β was allowed to vary between 0 and 180° at intervals of 30°. Table 1 lists the results of these calculations. The values of the energy are not absolute but refer to the calculated minimum energy value taken as zero.

TABLE 1

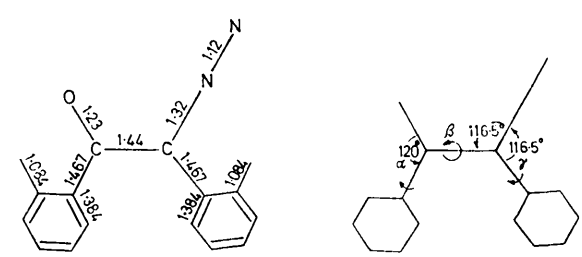
Energy values (kJ mol^{-1}) calculated for the molecule $PhCOC(Ph)N_2$

β (°)	α 0° γ 0°	α 0° γ 30°	α 0° γ 60°	α 0° γ 90°	α 30° γ 30°	α 30° γ 60°	α 30° γ 90°	α 60° γ 60°	α 60° γ 90°	α 90° γ 90°
0	*a*	42.8	172.5	122.2	*a*	185.7	14.2	178.6	172.8	261.2
30	119.8	*a*	704.2	145.3	135.2	292.2	97.6	177.4	193.9	227.8
60	50.6	90.4	332.0	150.9	64.9	86.2	102.6	185.9	197.0	267.3
90	37.0	48.2	76.0	91.6	55.4	75.5	86.3	170.2	180.0	319.6
120	8.0	16.0	36.3	46.8	31.8	49.3	57.6	149.8	157.0	356.1
150	0.0	6.5	23.9	33.2	29.1	44.9	52.4	144.2	150.5	429.8
180	42.8	47.2	61.9	70.7	21.1	36.2	44.7	159.1	166.0	269.6

[a] Variable.

From Table 1 it is seen that the forms with α 60, γ 60°; α 60, γ 90°; and α 90, γ 90° may be ignored, since, for constant β, these conformations have a higher energy than the other forms.

Table 1 shows that for any set of (α, γ) values the function $E = f(\beta)$ shows two minima: the first is always at $\beta = 0°$ (*cis*-conformer) except when both angles α and γ are 90°, in which case the minimum occurs at $\beta = 30°$, and the second minimum is found in part at $\beta = 180°$ (*trans*-conformer) and in part at $\beta = 150°$. The greater stability of the *cis*- and *trans*-forms (or very close to these) is due to the delocalisation of the π electrons of the



α 0; γ 0; β 0

FIGURE 1 Geometrical parameters and diagram of $PhCOC(Ph)N_2$ molecule used in calculations

[4] R. Cataliotti, G. Paliani, and S. Sorriso, *Spectroscopy Letters*, 1974, **7**(9), 449.

[5] G. Paliani, S. Sorriso, and R. Cataliotti, *J.C.S. Perkin II*, in the press.

[6] G. Piazza, S. Sorriso, and A. Foffani, *Tetrahedron*, 1968, **24**, 4751.

[7] S. Sorriso, G. Piazza, and A. Foffani, *J. Chem. Soc.* (*B*), 1971, 805.

[8] S. Sorriso and A. Foffani, *J.C.S. Perkin II*, 1973, 2142.

[9] S. Sorriso and A. Foffani, *J.C.S. Perkin II*, 1973, 1497.

[10] J. A. Pople and G. A. Segal, *J. Chem. Phys.*, 1966, **44**, 3289.

[11] QCPE program 141, Chemistry Department, Indiana University.

[12] QCPE program 136, Chemistry Department, Indiana University.

diazo-group over the CO–CN_2 molecular backbone, and this is at a maximum when the backbone is planar [see section (c)].

Apart from the conformations corresponding to the three pairs of (α, γ) values mentioned above, which were calculated to be the least stable, the difference between the energies of the minima of the function $E = f(\beta)$ for any pairs of (α, γ) values is always high. This indicates that two forms in equilibrium with the two phenyl groups in the same orientation are not possible. This is in agreement with conclusions drawn from molecular diagrams constructed with van der Waals atomic radii [13] and the structural parameters of Figure 1. There is probably an equilibrium between the *cis*-form with α 30, γ 90, and β 0° and a *trans*-one with β 150—180 and α and γ both 0°. Rotation about the phenyl-carbon bond also occurs during the interconversion between the two forms. The energy difference between these two forms is 14 kJ mol^{-1} and compares favourably with that (8.7 kcal mol^{-1}) calculated from measurements of integrated band intensities.[5] The electric dipole moment of benzoyl(diazo)phenylmethane [9] is compatible with either the presence of *cis*- and *trans*-forms in a 1 : 1 ratio or with a single very distorted species with β *ca.* 85°. From a theoretical point of view this second possibility may immediately be excluded since for no pair of (α, γ) values was a minimum found in the $E = f(\beta)$ function for *ca.* 85°.

The molecular conformation of benzoyl(diazo)phenylmethane is a compromise produced by several effects: (i) phenyl–carbonyl conjugation; (ii) phenyl–diazo-group conjugation; (iii) benzoyl–phenyldiazomethane conjugation; and (iv) steric and electrostatic effects between the two phenyls and between a phenyl and the diazo- or carbonyl group. The influence of all these effects may be deduced qualitatively from an examination of Table 1.

(i) *Interaction between the π system of the phenyl group and the π electrons of the carbonyl bond.* The amount of this interaction is evaluated by noting the behaviour of the molecular energies as a function of the angle α for conformations having the same angle β (120°, an angle at which the two phenyl groups do not interact sterically with one another) and the same γ angle (90°). The calculated values are (α/°, E/kJ mol^{-1}): 0, 46.8; 30, 57.6; 60, 157.0; 90, 356.1. This trend is essentially due to the decrease in phenyl–carbonyl conjugation with increase in α. In fact, the same behaviour is observed for γ angles different from 90°.

(ii) *Conjugation between the diazo-group and the adjacent phenyl group.* To see how important this effect is, as for (i), we examine the energies of the conformations for which β = 120 and α = 0° as a function of the angle γ. These give (γ/°, E/kJ mol^{-1}): 0, 8.0; 30, 16.0; 60, 36.3; 90, 46.8. The trend shows that there is interaction between the diazo and the phenyl groups. This may also be deduced from the frequencies of the N–N asymmetric stretching bands which lie at: diazoacetophenone 2 108, benzoyl(diazo)phenylmethane 2 071 and 2 088 cm^{-1}, recalling that the diazo group resonates mainly between the two extreme forms $=\overset{-}{C}-\overset{+}{N}\equiv N$ and $=C=\overset{+}{N}=\overset{-}{N}$. The increase in energy with increase in the angle of rotation of the phenyl (γ) is in this case smaller than that obtained by increasing α [point (i) above] for the phenyl group–carbonyl interaction. This is understandable if it is considered that the carbonyl group exerts a much larger $-I$ inductive effect and a $-M$ mesomeric effect on the phenyl group than does the diazo-group.

TABLE 2

Energy values (kJ mol^{-1}) calculated for the molecule $PhCOC(Me)N_2$

β (°)	γ 0° α 0°	γ 0° α 30°	γ 0° α 60°	γ 0° α 90°	γ 60° α 0°	γ 60° α 30°	γ 60° α 60°	γ 60° α 90°
0	303.7	38.0	166.4	269.8	0.0	31.4	167.2	269.6
30	14.1	45.4	190.7	226.7	40.4	44.3	190.1	230.2
60	15.7	68.6	237.2	259.8	21.5	68.3	195.0	265.7
90	35.3	67.8	178.3	332.4	34.7	67.5	178.0	327.3
120	20.9	43.2	175.4	397.9	20.8	43.4	155.3	369.6
150	9.7	39.5	158.6	441.0	10.2	39.8	149.4	413.3
180	58.4	30.5	165.9	267.4	59.0	31.1	166.5	272.3

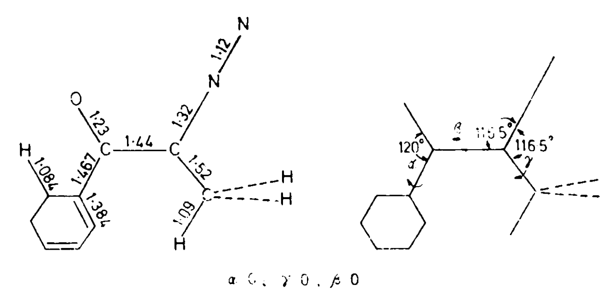


FIGURE 2 Geometrical parameters and diagram of $PhCOC(Me)N_2$ molecule used in calculations

(iii) *Benzoyl–phenyldiazomethane conjugation.* The presence of this conjugation is demonstrated by the fact that the minima are at β 0—30 and 150—180° for all the pairs of (α, γ) values.

(iv) *Steric and electrostatic effects.* It is not possible to separate these effects from those of point (iii) but it is evident from Table 1 that the steric repulsion between the two phenyls is greater than the electrostatic effects.

(b) 1-*Benzoyl*-1-*diazoethane*.—Calculations on this molecule were carried out following the scheme of Figure 2, keeping the angles and bond distances constant. Two series of calculations were performed: one for γ = 0° (one methyl hydrogen facing the phenyl group and the

[13] L. Pauling, 'The Nature of the Chemical Bond,' Cornell University Press, New York, 3rd edn., p. 260.

C–H bond in the CN_2 plane) and the other for $\gamma = 60°$. For each of these two values for the angle of rotation of the methyl group, the angle of rotation of phenyl (α) was allowed to vary between 0 and 90° at 30° intervals. For each pair of (α, γ) values, the rotation angle about the central C–C bond (β) was allowed to vary between 0 and 180° at 30° intervals. The results of these calculations are reported in Table 2. As for benzoyl(diazo)phenylmethane, the energy values are not absolute, but are referred to the minimum calculated value.

TABLE 3

Charge densities on the CO and CN_2 groups calculated for the molecules $PhCOC(Ph)N_2$ and $PhCOC(Me)N_2$

$PhCOC(Ph)N_2$

Atom	β (°) 0	30	60	90	120	150	180	α, γ (°)
C	*a*	5.64	5.68	5.69	5.71	5.71	5.72	
O		8.46	8.37	8.32	8.32	8.34	8.35	
C		5.95	6.05	6.08	6.10	6.10	6.10	0, 0
N		6.50	6.60	6.64	6.64	6.62	6.65	
N		7.44	7.31	7.27	7.23	7.22	7.17	
C	5.72	*a*	5.67	5.69	5.71	5.71	5.72	
O	8.35		8.38	8.33	8.32	8.34	8.35	
C	6.10		6.03	6.07	6.10	6.10	6.10	0, 30
N	6.65		6.60	6.65	6.65	6.63	6.66	
N	7.17		7.33	7.28	7.23	7.22	7.17	
C	5.66	5.64	5.66	5.68	5.70	5.71	5.72	
O	8.46	8.46	8.39	8.34	8.33	8.35	8.35	
C	5.97	5.94	6.01	6.06	6.09	6.09	6.10	0, 60
N	6.52	6.52	6.61	6.66	6.66	6.64	6.67	
N	7.40	7.45	7.36	7.31	7.25	7.23	7.18	
C	5.66	5.66	5.66	5.68	5.70	5.71	5.72	
O	8.45	8.44	8.39	8.34	8.33	8.35	8.35	
C	5.99	5.98	6.01	6.05	6.09	6.09	6.10	0, 90
N	6.54	6.56	6.62	6.66	6.66	6.64	6.68	
N	7.38	7.39	7.37	7.32	7.26	7.24	7.19	
C	*a*	5.69	5.71	5.72	5.73	5.73	5.73	
O		8.37	8.31	8.30	8.32	8.34	8.34	
C		6.05	6.08	6.10	6.11	6.10	6.10	30, 30
N		6.61	6.66	6.67	6.66	6.65	6.64	
N		7.28	7.25	7.23	7.21	7.19	7.20	
C	5.70	5.70	5.70	5.72	5.73	5.73	5.73	
O	8.41	8.37	8.32	8.30	8.32	8.34	8.34	
C	6.03	6.06	6.08	6.10	6.10	6.10	6.10	30, 60
N	6.59	6.63	6.67	6.68	6.67	6.66	6.65	
N	7.30	7.29	7.28	7.25	7.22	7.20	7.21	
C	5.70	5.70	5.70	5.72	5.72	5.73	5.73	
O	8.40	8.36	8.32	8.31	8.32	8.34	8.34	
C	6.06	6.06	6.07	6.09	6.10	6.10	6.10	30, 90
N	6.60	6.46	6.68	6.69	6.67	6.67	6.66	
N	7.29	7.29	7.28	7.26	7.23	7.26	7.21	
C	5.76	5.76	5.78	5.78	5.78	5.77	5.77	
O	8.32	8.27	8.25	8.27	8.30	8.31	8.29	
C	6.08	6.09	6.10	6.10	6.10	6.10	6.10	60, 60
N	6.69	6.72	6.73	6.71	6.70	6.71	6.73	
N	7.19	7.21	7.21	7.19	7.18	7.17	7.18	
C	5.76	5.76	5.78	5.78	5.78	5.77	5.77	
O	8.31	8.27	8.25	8.27	8.30	8.31	8.29	
C	6.08	6.09	6.10	6.10	6.10	6.10	6.10	60, 90
N	6.70	5.73	6.73	6.72	6.71	6.71	6.73	
N	7.20	7.22	7.22	7.20	7.18	7.18	7.19	
C	6.19	6.17	6.11	6.02	5.94	5.82	6.18	
O	8.11	8.13	8.13	8.14	8.16	8.24	8.10	
C	5.87	5.90	5.93	5.98	6.00	6.00	5.89	90, 90
N	6.70	6.69	6.69	6.72	6.78	6.83	6.74	
N	7.09	7.07	7.10	7.14	7.17	7.21	7.08	

TABLE 3 (*Continued*)

$PhCOC(Me)N_2$

Atom	β (°) 0	30	60	90	120	150	180	α, γ (°)
C	5.73	5.73	5.73	5.73	5.73	5.73	5.74	
O	8.35	8.34	8.30	8.28	8.29	8.32	8.33	
C	6.16	6.16	6.16	6.16	6.16	6.16	6.16	0, 0
N	6.67	6.68	6.70	6.70	6.71	6.69	7.71	
N	7.11	7.12	7.14	7.16	7.14	7.13	7.10	
C	5.74	5.74	5.75	5.75	5.75	5.75	5.74	
O	8.34	8.30	8.27	8.27	8.30	8.32	8.32	
C	6.16	6.16	6.16	6.16	6.15	6.15	6.15	30, 0
N	6.68	6.70	6.72	6.72	6.71	6.70	6.70	
N	7.11	7.13	7.15	7.15	7.14	7.12	7.12	
C	5.77	5.78	5.79	5.79	5.78	5.78	5.77	
O	8.30	8.25	8.23	8.26	8.29	8.30	8.28	
C	6.13	6.12	6.13	6.13	6.12	6.12	6.12	30, 0
N	6.72	6.74	6.74	6.72	6.72	6.73	6.74	
N	7.13	7.16	7.16	7.14	7.13	7.13	7.14	
C	6.20	6.18	6.11	6.02	5.95	5.82	6.15	
O	8.10	8.12	8.13	8.14	8.14	8.24	8.09	
C	5.89	5.91	5.94	5.99	6.01	6.01	5.89	90, 0
N	6.72	6.71	6.71	6.74	6.78	6.83	6.75	
N	7.04	7.02	7.05	7.09	7.14	7.18	7.05	
C	5.73	5.73	5.73	5.73	5.73	5.73	5.74	
O	8.35	8.33	8.30	8.28	8.29	8.32	8.33	
C	6.16	6.16	6.16	6.16	6.16	6.15	6.14	0, 60
N	6.67	6.68	6.70	6.71	6.71	6.69	6.71	
N	7.11	7.12	7.15	7.16	7.15	7.13	7.10	
C	5.74	5.74	5.75	5.78	5.75	5.75	5.74	
O	8.34	8.30	8.27	8.27	8.30	8.32	8.32	
C	6.16	6.16	6.16	6.16	6.15	6.14	6.15	30, 60
N	6.68	6.70	6.72	6.72	6.71	6.70	6.70	
N	7.11	7.14	7.16	7.15	7.14	7.12	7.12	
C	5.77	5.78	5.79	5.79	5.78	5.78	5.77	
O	8.29	8.25	8.29	8.26	8.29	8.30	8.28	
C	6.13	6.13	6.13	6.13	6.13	6.12	6.12	60, 60
N	6.72	6.74	6.74	6.73	6.72	6.73	6.74	
N	7.13	7.16	7.16	7.15	7.13	7.13	7.15	
C	6.20	6.17	6.11	6.01	5.94	5.85	6.15	
O	8.10	8.12	8.12	8.14	8.15	8.20	8.08	
C	5.89	5.91	5.94	5.99	6.01	6.01	5.90	90, 60
N	6.72	6.71	6.71	6.74	6.78	6.48	6.75	
N	7.05	7.02	7.05	7.10	7.14	7.19	7.06	

[a] Variable.

Table 2 shows that, for constant γ and β angles, the conformations having higher energies are those with α 60 and 90°, whilst the theoretically more stable conformations arise when α 30 and 0°, thus indicating that the phenyl group is conjugated with the carbonyl function [see section (c)].

Consider the two series of conformations with α 0, γ 0° and α 0, γ 60° (Table 2). The energy of each conformation of the first series is of the same order as the corresponding one of the second having the same angle β, except for β 0 and 30°. This is due to the steric effect exerted by the methyl hydrogen on the *o*-hydrogen of the phenyl ring. The difference between the two minima for α 0, γ 0° is 3.0 kJ mol^{-1}. For α 0, γ 60°, there are three minima. The difference between two of these minima is not more than 12.0 kJ mol^{-1}. The energy barrier height to interconversion is 26.0 kJ mol^{-1} for α 0, γ 0° and 40.0 and 27.0 kJ mol^{-1} for α 0, γ 60°. The barrier height to free internal rotation about the central

C–C bond is 300.0 in the former and 49.0 kJ mol^{-1} in the latter case. The results allow us to suggest that there is free, or only partially restricted, internal rotation about the C–C bond in this molecule. Free internal rotation is possible only if there is simultaneous rotation about the Me–C bond, a result in agreement with the i.r. spectrum,[4,5] which shows only a single band arising from the N–N asymmetric stretching vibration. Free rotation about the central C–C bond was not considered in previous work[8] on the basis of the results obtained for diazoacetophenone and its *para*-substituted derivatives.[7] In fact, for these molecules only a form with the diazo and carbonyl groups in the same plane and *cis* to one another was found. Now we can suggest that the reason why there is no free or restricted internal rotation about C–C bond in α-diazoacetophenones lies in the fact that they are strongly stabilised by the conjugation between the diazo and carbonyl groups. For the molecule $PhCOC(Me)N_2$ this stabilisation is balanced by the greater steric effect that increases the energy of the planar forms towards values similar to those for the non-planar ones.

(c) *Charge Densities*.—Charge densities on the CO and CNN groups are reported in Table 3 from which it may be seen that the charge density is a maximum for β 0 and 180° and a minimum for β *ca*. 90°. The difference between the charge density on the CN_2 group at β 0 (180°) and at β 90° is greater for α 90 than for α 0°. This indicates that for low values of the angles β and γ the CO group conjugates with the CN_2 group and the phenyl ring, respectively. These results are in good agreement with those obtained from the energy values.

Conclusions.—Benzoyl(diazo)phenylmethane shows two energy minima at similar energies and may, according to these theoretical calculations, exist in two configurations. The *cis* $\rightleftharpoons$ *trans*-interconversion is rather slow because of the high energy barrier between the two forms. During this process, the two phenyls rotate about the bond with the rest of the molecule. By contrast, for 1-benzoyl-1-diazoethane the barrier to rotation about the central C–C bond is small and should allow rapid interconversion between the rotamers or free rotation. The phenyl group remains more or less in the same plane as the $COCN_2$ group, whilst it is the methyl that rotates. This agrees with the values for the energy barriers to rotation about C–Ph and C–Me bonds.

These conclusions are in good agreement with the observed dipole moments and with the i.r. spectral data.

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